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# Visible Light-Promoted Regioselective Benzannulation of Vinyl Sulfoxonium Ylides with Ynoates

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**ABSTRACT:** Herein, we report a highly regioselective [4 + 2]-annulation of vinyl sulfoxonium ylides with ynoates under light-mediated conditions. The reaction proceeds through the new dienyl sulfoxonium ylide, which undergoes photolysis under blue light irradiation to give highly substituted naphthalene scaffolds. The method presented here operates at room temperature and does not require the addition of an external photosensitizer. The *in situ*-generated dienyl sulfoxonium ylide absorbs light and acts as a photosensitizer for the formation of arenes. The synthetic potential of these benzannulations was further illustrated by various synthetic transformations and a scale-up reaction. Moreover, control experiments and quantum chemical calculations reveal the mechanistic details of the developed reaction.

**KEYWORDS:** *regioselective annulations, sulfur ylides, photochemistry, arenes, alkynes, benzannulation*
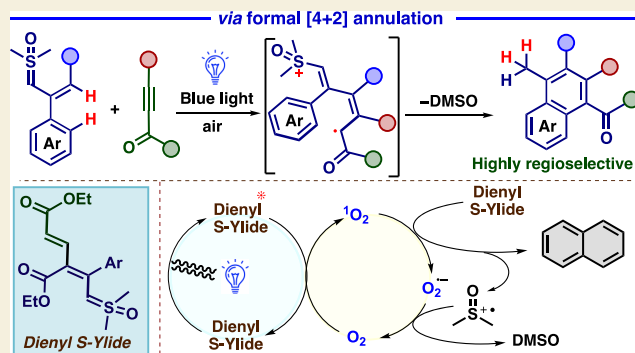
## ■ INTRODUCTION

Substituted naphthalenes are important and ubiquitous scaffolds in many natural products,[1] bioactive molecules,[2] nanomaterials,[3] ligands for transition metals,[4] and other materials with useful properties (Figure 1).[5,6] The synthesis of substituted naphthalenes encompasses a vast number of approaches.[7,8]
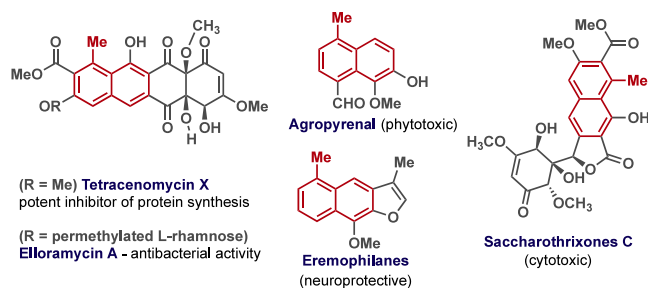


**Figure 1.** Methylated naphthalene core in bioactive natural products.

The dehydro-Diels−Alder (DDA) reaction is one of the most powerful reactions to construct highly substituted arenes.[9] The straightforward approach for the naphthalene scaffolds via the intermolecular DDA reaction is challenging because of the high activation energy (Scheme 1a). Since 1963, intramolecular didehydro-Diels−Alder (IMDDA) reactions of styrene-ynes to construct naphthalenes have attracted much attention (Scheme 1b).[10] However, the IMDDA reaction required harsh reaction conditions, which often resulted in the polymerization of

styrene. The recent renaissance of photocatalysis provides a new space for various styrene-based [4 + 2] annulations.[11−14] In 2018, Lei's group developed a visible-light-mediated [4 + 2] annulation reaction between styrene derivatives with alkynes to generate naphthalenes by using an acridinium photosensitizer and cobalt catalyst (Scheme 1c).[15] Despite the success of various light-mediated [4 + 2] annulations, these methods encounter certain inherent challenges: (1) The reactions can give the [2 + 2] cycloaddition instead of [4 + 2]-annulation according to the Woodward−Hoffmann rules, (2) to generate the key radical cation intermediate, the reaction usually requires both electron-rich diene and dienophile components, (3) the regio- and stereoselectivities are the main challenges for the intermolecular additions, (4) homodimerization is also another feasible transformation under these conditions, and (5) these methods require expensive metal and organophotoredox catalysts. Thus, it is desirable to develop an efficient, regioselective, catalyst-free intermolecular light-mediated [4 + 2] annulation to address these issues.

Recently, the catalyst-free generation of carbenes from the diazo compounds (absorption >400 nm) under blue light has
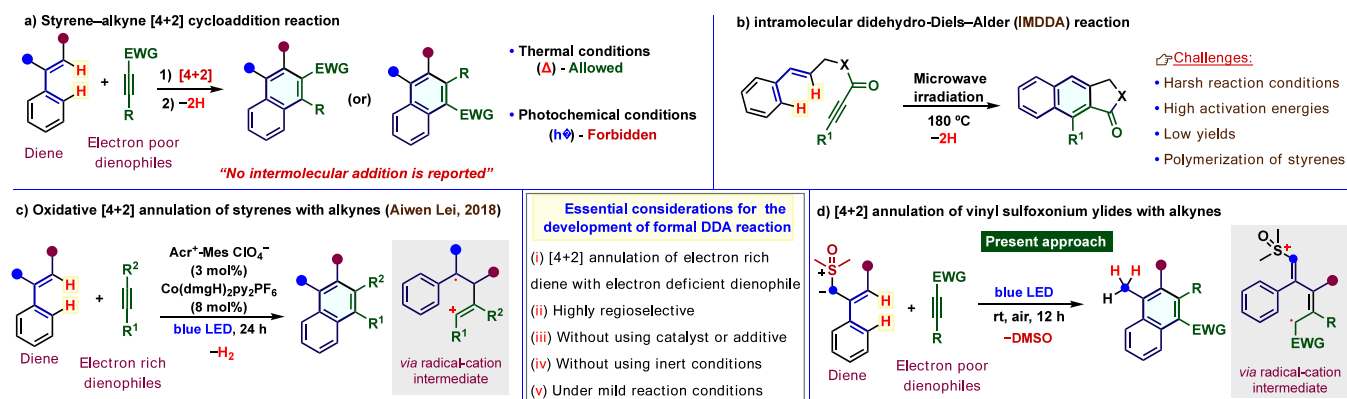
**1073**

**Scheme 1. Synthesis of Substituted Naphthalenes from Alkynes and Styrene derivatives**



**Scheme 2. Synthesis of Substituted Arenes from Vinyl Sulfoxonium Ylides**



proven to be a valuable alternative approach to transition metal catalysis. This approach provides a straightforward and general platform for various carbene transfer reactions with different trapping reagents under mild conditions (Scheme 2a).[16−21] Moreover, most of the light-mediated diazo-based transformations follow a reaction pathway similar to that of metal-catalyzed reactions.

Sulfoxonium ylides are alternatives to diazo compounds in carbene transfer reactions due to their advantages of operational safety, and high thermal stability.[22−25] However, like diazo-based catalyst-free photochemical transformations, the chemistry of sulfoxonium ylides has not been explored under visible light.[26−28]

The major challenges associated with the light-mediated conversion of sulfoxonium ylides are the light absorption of ylides as well as the leaving ability of DMSO (Scheme 2b).[29] As part of our ongoing research interest in sulfur ylides[30−37] and intrigued by metal-free carbene generation from diazo compounds, we would like to explore the reactivity of vinyl sulfoxonium ylide in the presence of blue light to open up a new avenue of sulfoxonium ylide based photochemistry.[38−40]

Initially, we wanted to perform our previously reported metal-catalyzed vinyl carbene-mediated [4 + 2] benzannulation in the presence of blue light (Scheme 2c, expected pathway).[34] Thus, we began our investigation with the reaction of 0.3 mmol of vinyl sulfoxonium ylide **1** (obtained in one step from 1 mmol of ynoate and 1.4 mmol of dimethylsulfoxonium methylide) and 0.4 mmol of methyl propiolate (**2**) in DCE at 427 nm. Surprisingly, the reaction gave the naphthalene scaffold **3** instead of the expected arene **3′**. Initial mechanistic studies reveal that the reaction proceeds through the intermediate dienyl sulfoxonium ylide (**int-A**), which can act as a sensitizer (see the SI, Figure 5). This serendipitous outcome prompted us to explore the styrene-yne [4 + 2] annulation, which has been difficult to achieve by the traditional intermolecular DDA reaction.[41] In this work, we have developed a highly regioselective [4 + 2] annulation of vinyl sulfoxonium ylides with terminal and internal ynoates to generate highly substituted naphthalenes under blue light conditions (Scheme 1d).

## ■ RESULTS AND DISCUSSION

We optimized the present [4 + 2] annulation by using various protic/aprotic solvents and photocatalysts (for the optimization, see the Supporting Information, Table 1), and the reaction gave good yields of naphthalene **3** in ethanol at rt. Interestingly, the reaction does not require any external photocatalyst or additive.[42,43] To explore the substrate scope of the reaction, we examined the different substitutions at the aryl ring of the vinyl sulfoxonium ylide (Scheme 3). A variety of aryl groups bearing electron-donating, electron-neutral, and halogen groups at *meta-* and *para-* positions underwent the [4 + 2] annulation with methyl propiolate to afford the corresponding naphthalenes **3a−3h** in 58−68% yields. Moreover, the structure of product **3b** was confirmed by using X-ray analysis (CCDC 2271065). The substitution at the *ortho-* position of the aryl group of the ylide gave a low yield of naphthalene **3i** due to the lower stability of the ylide. Then, we evaluated the variation in the ester part of ylide **1**. The ester group containing 2-(trimethylsilyl)ethyl, benzyl, and cyclohexyl substitutions provided the naphthalenes **3j−3l** in 54−60% yields, respectively. The efficiency of this method was further demonstrated through the variations in dienophile **2**. A series of ynoates, such as cyclohexyl, allyl, and propargylic substitution at the ester, underwent [4 + 2] annulation and yielded arenes **3m−3p** in 34−52% yields.

Next, we evaluated the scope of the internal alkynes. The reaction of various aryl-substituted vinylsulfoxoniums with diethyl acetylenedicarboxylate gave naphthalene triesters **3q−**

**Scheme 3. Scope of Blue Light Promoted Benzannulation of Vinyl Sulfoxonium Ylide with Terminal and Internal Alkynes[a,b]**
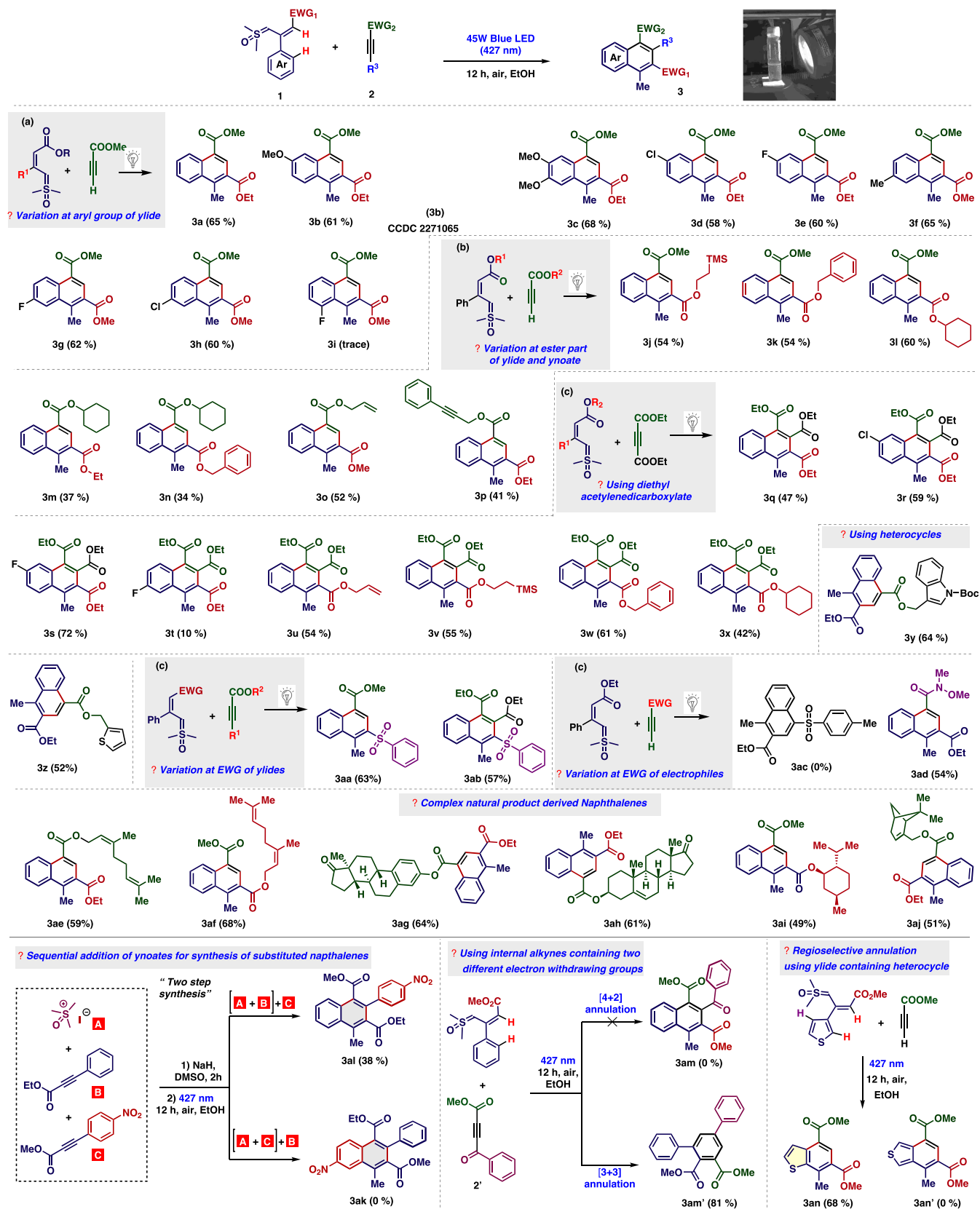
[a]Reaction conditions: **1** (0.4 mmol), **2** (0.5 mmol), in ethanol (0.2 M) under open air conditions at rt and light irradiation from 427 nm Kessil lamp (45W) for 12 h. [b]Isolated yields of naphthalenes **3**.

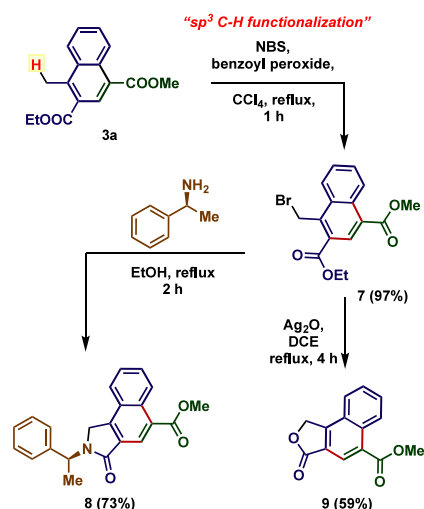**Scheme 4. Synthetic Applicability of the Developed [4 + 2] Annulation**



a) Precursor preparation for the fluorescent whitening agent for polyester fibers and plastics
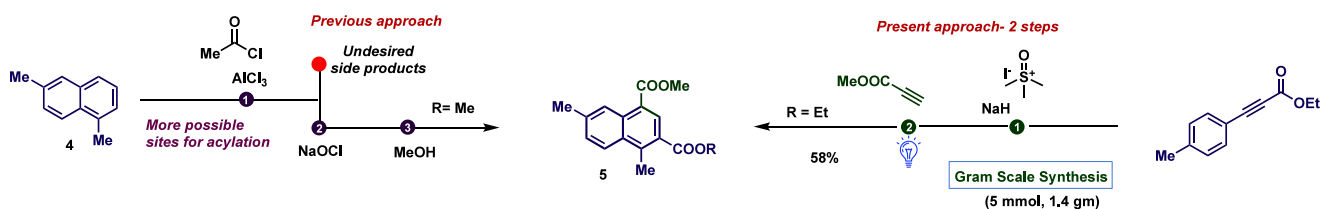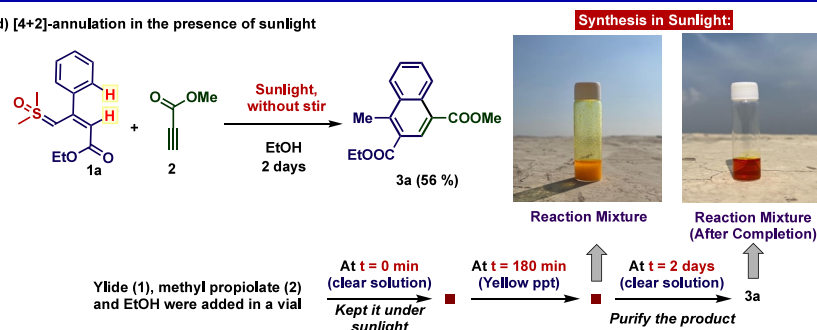
b) Two step synthesis of naphthalactone from vinyl sulfoxonium ylide
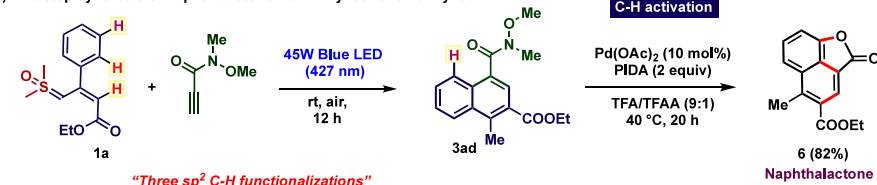
c) Conversion of methyl group in 3a

d) [4+2]-annulation in the presence of sunlight

**3t** in 10−72% yields. This reaction is also successful with variation at the ester part of the ylide and gave **3u**−**3x** in 42−61% yields. The reaction is also successful with the ynoates containing heterocyclic scaffolds and yielded the products **3y** and **3z** in 64% and 52% yields, respectively. Moreover, the reaction is also successful with the sulfonyl group-stabilized vinyl sulfoxonium ylide and yielded the naphthalene **3aa** and **3ab** in 63% and 57% yield, respectively.

Attempts to perform this reaction with other electron-deficient alkynes such as tosyl acetylene were not successful. Notably, this reaction is also successful with the *N*-methoxy propiolamide and gave the Weinreb amide-substituted naphthalene **3ad** in 54% yield. This scaffold can be utilized as a precursor for various transformations to obtain biologically active molecules.[44]

The robustness of this protocol was demonstrated with structurally complex ynoates and ylides containing steroid and terpenoid derivatives yielding the desired naphthalenes **3ae**−**3aj** in 49−68% yields. Subsequently, we investigated the synthesis of naphthalenes from two different aryl propiolates. The addition of dimethylsulfoxonium methylide generated from the salt (A) on ethyl phenylpropiolate (B) followed by treatment with the methyl 4-nitrophenylpropiolate (C) gave naphthalene **3al**, albeit in a lower yield (38%). However, switching the propiolate sequence could not afford desired product **3ak**. Interestingly, the reaction between ylide and internal alkynes containing keto and ester groups afforded *meta*-terphenyls **3am'** as the exclusive product instead of substituted naphthalene **3am** (see the SI, Scheme 6.1). When we treated thiophene-derived vinyl sulfoxonium ylide with methyl propiolate under standard conditions, the reaction exclusively afforded benzothiophene derivative **3an** in 68% yield. Surprisingly, another possible

regioisomer benzo[c]thiophene derivative **3an'** is not observed in this transformation. Moreover, the [4 + 2] annulation of pyridine-derived vinyl sulfoxonium ylide with methyl propiolate is unsuccessful.

To demonstrate the potential of this developed method, a scale-up reaction was performed for constructing the important naphthalene scaffold **5**, which can be used as a precursor for the polyester fiber (Scheme 4a).[45] In the reported approach, product **5** was obtained from the pre-existing naphthalene unit **4** by Friedel−Crafts acylation, which gave possible side products along with the desired product. To our delight, the 5 mmol scale of the present annulation under standard reaction conditions afforded naphthalene **5** in 58% yield in two steps from the ynoate. Subsequently, we synthesized naphthalactone **6** in 82% yield from vinyl sulfoxonium ylide in two steps by three sp² C−H functionalizations on ylide **1a** (Scheme 4b). First, naphthalene scaffold **3ad** was generated from the vinyl sulfoxonium ylide with propiolamide. Then, **3ad** undergoes a palladium-catalyzed C8-oxygenation/lactonization sequence using Weinreb amide as a directing group to generate naphthalactone **6** (Scheme 4c).[46] Next, we performed radical mediated bromination on **3a** to generate naphthyl bromide **7** in 97% yield. The reaction of **7** with (S)-phenylethylamine gave lactam **8** in 73% yield. In addition, subjecting naphthyl bromide **7** under silver-mediated conditions led to intramolecular lactonization to give lactone **9**. Notably, the present benzannulation was performed in sunlight for 2 days and gave the desired naphthalene **3a** in 56% yield (Scheme 4d).

Several mechanistic experiments were conducted to elucidate the present benzannulation (Scheme 5). The reaction of vinyl sulfoxonium ylide **1** with ynoate **2** in the absence of light gave the dienyl sulfoxonium ylide **10**.[47,48] The structure of ylide **10** was

## Scheme 5. Mechanistic investigation for [4 + 2] Benzannulation
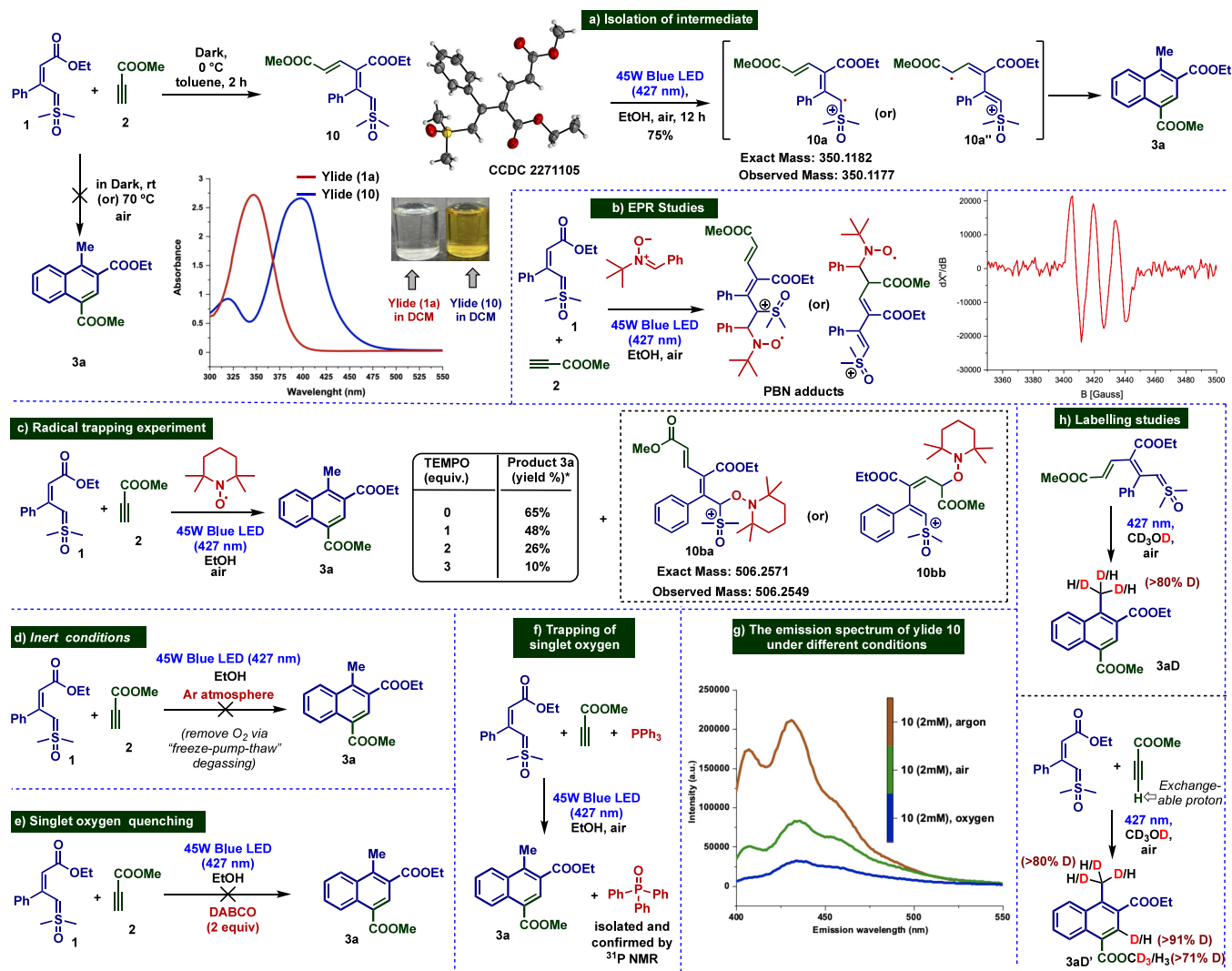
confirmed using X-ray analysis (CCDC 2271105). Next, the reaction of **10** in the presence of blue light gave arene **3a** in 75% yield (Scheme 5a). The light irradiation is essential to the transformation because **3a** could not be detected when the reaction is performed in the dark at room temperature or heated at 70 °C. The UV−vis absorption spectra of vinyl sulfoxonium ylide **1** showed absorption around the 330 nm region. However, dienyl sulfoxonium ylide **10** showed appreciable absorption around the 400 nm region. This indicates that the $\pi$−conjugation extended ylide is the key component in the light-mediated reaction. To investigate the involvement of radicals in the mechanism, we performed EPR studies using *N-tert*-butyl-$\alpha$-phenylnitrone (PBN) as a radical trap in the present reaction, which clearly showed the generation of radical species (Scheme 5b).

Next, we performed the reaction with radical trapping agents such as TEMPO. The gradual decrease in the yield of **3a** is observed by increasing the concentration of TEMPO (Scheme 5c). Moreover, the TEMPO-captured intermediates are detected by HRMS, which further supports that a radical pathway is involved in the catalytic cycle. When the reaction was performed under argon, the reaction was completely shut down, suggesting the role of O₂ (Scheme 5d). Additionally, the introduction of DABCO, an inhibitor of ¹O₂, suppressed the

formation of product **3a**, indicating the presence of singlet oxygen species in the reaction process (Scheme 5e). To further prove the presence of photoexcited singlet oxygen, trapping experiments were performed using triphenylphosphine under the standard conditions and afforded the triphenylphosphine oxide as a side product, which formed through a peroxide intermediate, while the corresponding oxidation was not detected in the dark (Scheme 5f).[49] This reaction clearly indicates that ¹O₂ is produced from air under irradiation. The fluorescence emission quenching study showed that the emission intensity of excited ylide **10** was remarkably affected by O₂ (Scheme 5g). In addition, the cyclic voltammetry (CV) analysis reveals that the ylide **10** (−1.46 V vs SCE) can reduce the oxygen (−0.75 V vs SCE) to generate the radical ion **10a** (see Supporting Information, Figure 12). Next, the reaction was conducted in CD₃OD instead of EtOH. The deuteration took place at the ylidic carbon suggesting that the solvent could be a proton source for this reaction (Scheme 5h).

To further understand the mechanistic details, density functional theory (DFT) calculations were carried out at the B3LYP-D3(BJ)/6-311++G(d,p)/SMD (ethanol) | B3LYP/6-31G(d) level of theory using Gaussian 09 Revision D.01. software. In the present annulation (Scheme 6), the radical intermediate **int-1A** cyclizes via **TS-1A** with an energy barrier of

## Scheme 6. Computed Energy Profile (in kcal/mol) for [4 + 2] Annulation
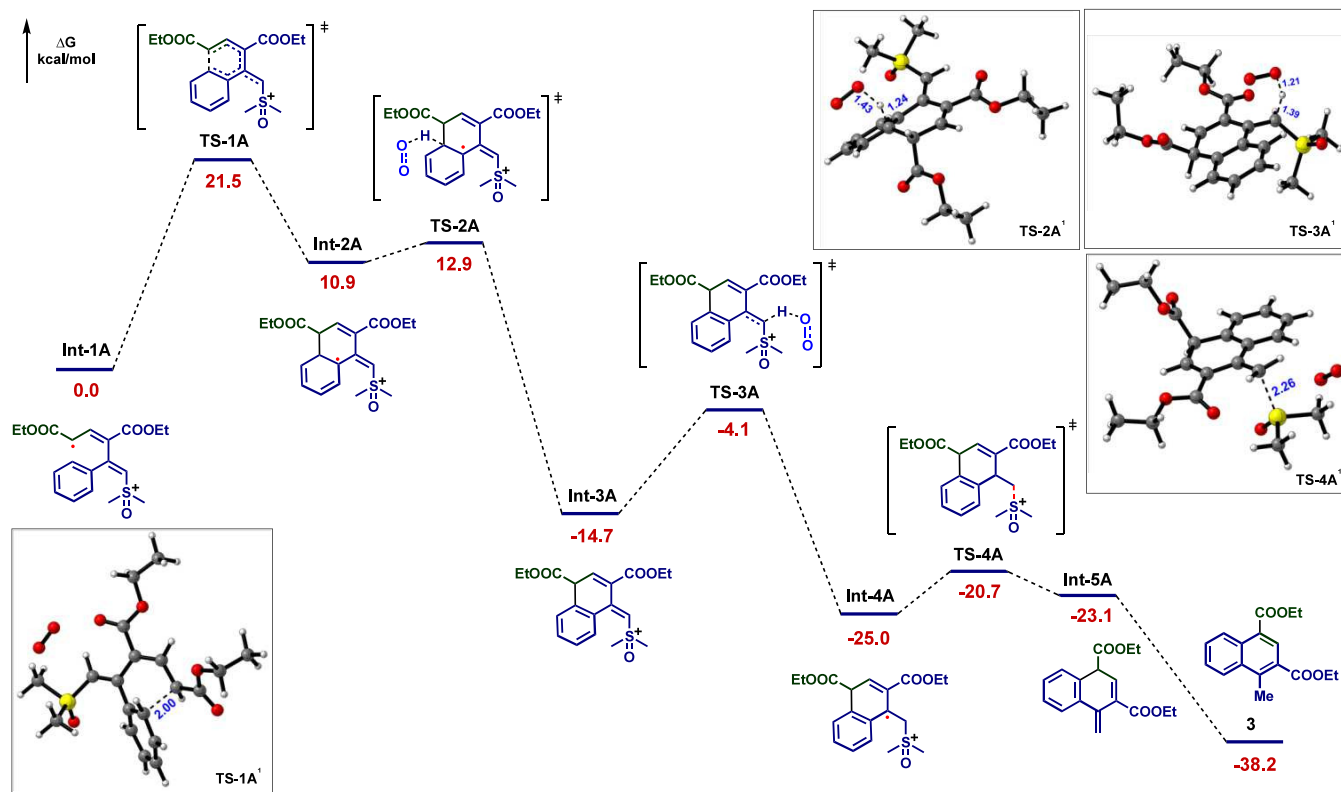


## Scheme 7. Plausible Mechanism for [4 + 2] Benzannulation
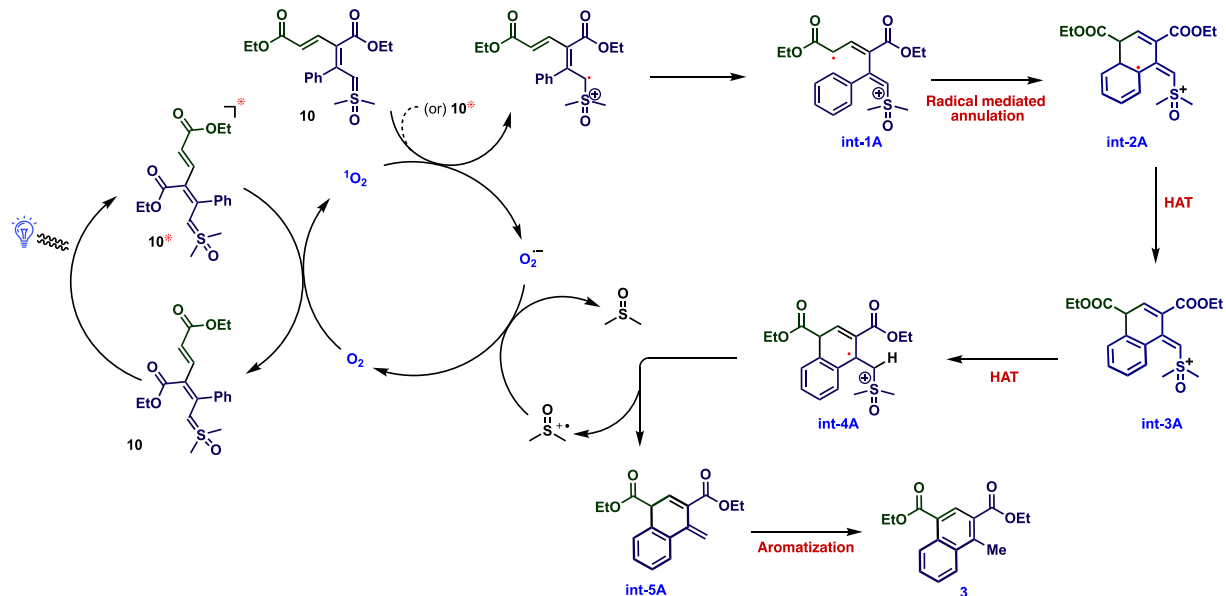


21.5 kcal/mol and generates the **int-2A**. Energetics shows that this is the slowest step in the reaction mechanism. **Int-2A** undergoes H-radical abstraction promoted by the singlet oxygen to form **int-3A** via **TS-2A** (12.9 kcal/mol). Transferring the abstracted H-radical to the ylide carbon of **int-3A** leads to **int-4A**, which shows significant stability as the generated radical is at the benzylic and allylic positions. Subsequently, the DMSO radical cation is released from **int-4A** by homolytic cleavage forming **int-5A**. This step does not require high energy, as it

entails the production of a neutral molecule that aromatizes directly into the final product, **3**.

Based on the experimental and theoretical investigations and previous reports on singlet oxygen-mediated photochemical reactions,[50] the plausible mechanism for the [4 + 2] annulation is proposed in Scheme 7. The excited sulfoxonium ylide **10*** is capable of converting $^3O_2$ to $^1O_2$, which can oxidize either **10** or **10*** via the SET process to generate **int-1A**. The radical-mediated annulation of **int-1A** gives **int-2A**, which can undergo sequential hydrogen atom transfer to give **int-4a.** Then

elimination of the DMSO radical cation from **int-4a** gives **int-5A**, which further aromatizes to produce the arene **3**. The released DMSO radical cation oxidizes the superoxide ion to the resulting ionic reagent, $O_2$.

## CONCLUSIONS

In conclusion, we have developed the first catalyst and additive-free blue-light-mediated transformations of sulfoxonium ylides. The reaction affords various highly substituted naphthalene scaffolds via [4 + 2] annulation of vinyl sulfoxonium ylides with ynoates. In this approach, the *in situ*-generated novel dienyl vinyl sulfoxonium ylide can act as a photosensitizer. This method offers several key advantages, including mild reaction conditions, broad substrate scope, operational simplicity, high regioselectivity, high scalability, and the ability to facilitate late-stage modifications. Detailed computational and experimental studies reveal that the reaction proceeds through a ylide-based radical cation intermediate. Sulfoxonium ylides are frequently employed as synthetic alternatives to diazo compounds in metal-catalyzed transformations owing to their similar reactivity. Sulfoxonium ylides are regarded as synthetic equivalents of diazo compounds and have been widely used as carbene surrogates in organic transformations under transition-metal catalysis. Unlike diazo compounds, it was observed that the excited dienyl sulfoxonium ylide did not undergo photolytic cleavage of DMSO to generate a carbene under visible light. However, the ylide involved in an energy transfer event with $O_2$ led to a completely different reaction path. This difference could be attributed to the leaving tendency of DMSO compared to $N_2$. Similar to the catalyst and additive-free visible light-mediated diazo transfer reactions, the present alkenyl sulfoxonium ylide can open up new windows in the photochemistry of ylide-based transformations to generate novel organic transformations.

## METHODS

To an oven-dried, 10 mL reaction vial equipped with a magnetic stir bar are added vinyl sulfoxonium ylide **1** (1 equiv, 0.4 mmol) and ynoate (1.2 equiv, 0.5 mmol) in 5 mL of ethanol as solvent. The vial was then irradiated using a 427 nm Kessil lamp at 6 cm from the light for 12 h. Then evaporate the solvent under reduced pressure. Then, the crude reaction mixture was loaded directly on silica (Biotage SNAP Ultra Samplet 10 g) and purified by flash column chromatography.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.3c00802.

  Representative experimental procedures, characterization and spectral data (NMR, HRMS), crystallographic data for **3b** and **10**, and DFT calculations (PDF)
  Crystallographic data for **3b** and **10** (CIF)
  Crystallographic data for **10** (CIF)

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https://pubs.acs.org/10.1021/jacsau.3c00802

### Author Contributions

D.S.D., D.K.G, and S.K, conducted the experimental investigation under J.V.'s supervision. D.K.G. and Anmol performed computational investigation under T.K.'s supervision. D.S.D, D.K.G., T.K., and J.V. wrote the manuscript. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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