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Photoinduced oxidative cyclopropanation of ene-ynamides: synthesis of 3-aza[*n*.1.0]bicycles *via* vinyl radicals†

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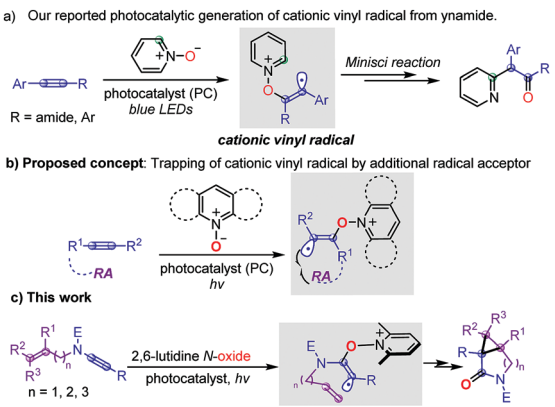
The first photoinduced synthesis of polyfunctionalized 3-aza[*n*.1.0] bicycles from readily available ene-ynamides and 2,6-lutidine *N*-oxide using an organic acridinium photocatalyst is reported. Applying a photocatalytic strategy to the reactive distonic cation vinyl radical intermediate from ynamide, a series of bio-valuable 3-azabicycles, including diverse 3-azabicyclio[4.1.0]heptanes and 3-azabicyclo[5.1.0] octanes that are challenging to accomplish using traditional methods, have been successfully synthesized in good to high yields under mild and metal-free conditions. Mechanistic studies are consistent with the photocatalyzed single-electron oxidation of ene-ynamide and the intermediacy of a putative cationic vinyl radical in this transformation. Importantly, this strategy provides new access to the development of photocatalytic vinyl radical cascades for the synthesis of structurally sophisticated substrates.

Ynamides are exceptionally versatile building blocks for the synthesis of diverse organic molecules, especially nitrogen containing structures and *N*-heterocycles.[1] The conjugation and polarization effects afforded by the amide group in ynamides allows for the development of highly efficient and selective new reactions and synthetic sequences.[1–3] For example, a variety of transition metal- or Brønsted acid-catalyzed selective addition reactions of ynamides with diverse nucleophiles have been studied extensively.[1,2] Ynamides with the polarized π-system have recently emerged as valuable α-oxo metal carbene precursors through transition metal-catalyzed oxygenative transformations with N–O bond oxidants.[3]

Alternatively, radical-mediated ynamide transformations present complementary and appealing synthetic approaches for the construction of carbon–carbon and carbon–heteroatom bonds that otherwise would be difficult to accomplish using traditional ynamide chemistry.[4] Nevertheless, such reactions, especially those catalyzed by photocatalysis, have been relatively less explored.[5] Recently, our group demonstrated convenient and catalytic access to the reactive distonic cation vinyl radical intermediate through a mild photocatalyzed single-electron oxidation of ynamides and arylacetylenes in the presence of pyridine *N*-oxide (Scheme 1a).[6,7] Accordingly, a visible-light photocatalyzed *ortho*-alkylation reaction of pyridine *N*-oxide with alkynes was developed. In this transformation, the pyridine *N*-oxide functioned as an oxygen transfer agent and a trapping substrate of the oxypyridinium tethered vinyl radical intermediate, which underwent an intramolecular Minisci-type pathway leading to the *ortho*-alkylation product.

We thus questioned whether the cationic vinyl radical intermediate could react with additional radical acceptor to initiate tandem radical transformations instead of engaging in the intramolecular Minisci reaction (Scheme 1a). In this regard, we envisioned that an alkene substituent in the ene-ynamide could serve as a viable radical-trapping unit for the photocatalytically



Scheme 1 (a) Our reported photocatalytic generation of vinyl radicals from ynamides. (b) Proposed concept. (c) This work.

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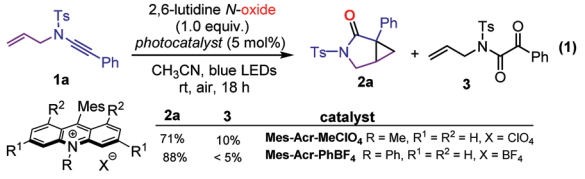
generated vinyl radical intermediate (Scheme 1b). Additionally, we hypothesized that the use of an *ortho*-substituted pyridine *N*-oxide, such as 2,6-lutidine *N*-oxide, could suppress the competing Minisci reaction. Following radical cascades, formal cyclopropanation, and N–O bond scission would release 2,6-lutidine and lead to a 3-aza[*n*.1.0]bicyclic skeleton. These highly functionalized motifs are commonly found in natural products, bioactive compounds, and important synthetic intermediates.[8] The construction of 3-azabicyclo[3.1.0]hexanes has been studied in a variety of reactions.[9] However, catalytic synthesis of 3-azabicyclo[4.1.0]heptanes and 3-azabicyclo[5.1.0]octanes is relatively rare and its development is in great demand.[10] Noteworthily, to the best of our knowledge, a catalytic photoredox synthetic methodology to 3-azabicyclo[*n*.1.0]hexanes has never been reported. In this context, we describe here a photoinduced oxygenative cyclopropanation of ene-ynamides for the synthesis of a series of 3-aza[*n*.1.0]bicycles *via* catalytically generated cationic vinyl radicals with 2,6-lutidine *N*-oxide as an oxygen donor. This methodology represents not only the first photocatalytic approach of 3-aza[*n*.1.0]bicycle synthesis, but also a complementary metal-free method with mild reaction conditions and general scope to the traditional transition metal-catalyzed processes.

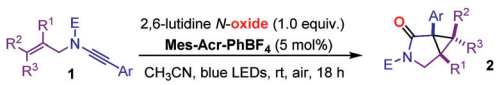


To test our hypothesis, the model substrate, *N*-allylynesulfonamide **1a**, was subjected to 5 mol% of 9-mesityl-10-phenyl acridinium perchlorate (Mes-Acr-MeClO$_4$) and 2,6-lutidine *N*-oxide (1.0 equiv.) in acetonitrile with blue LED light irradiation (λ_{max} = 450 nm) at room temperature (eqn (1)). As proposed, the 3-azabicyclo[3.1.0]hexane-2-one **2a** was generated smoothly in 71% yield under aerobic conditions. A ketoimide compound **3** was isolated in 10% yield, which is speculated to be generated from over-oxidation of the vinyl radical intermediate. Visible-light irradiation and the acridinium photocatalyst were indispensable for the reaction (Table S1, ESI†). Systematic examination of the reaction variants, including photocatalysts, *N*-oxides, and solvents, was performed (Table S1, ESI†). The optimized reaction conditions were identified with the use of 9-phenyl substituted acridinium[11] Mes-Acr-PhBF$_4$ and 2,6-lutidine *N*-oxide in acetonitrile, providing the best results to date under aerobic conditions (18 hours, 88% yield, and eqn (1)). Notably, under the standard conditions, but in the absence of oxygen, product **2a** was obtained, however, in lower yield (52%) under a prolonged reaction time (48 h), suggesting that dioxygen may play an important role in the regeneration of the photoredox catalyst.

Applying the optimized conditions, a variety of *N*-allylynamides with various substitution patterns and functional groups were subjected to the photocatalyzed intramolecular cyclopropanation reaction. The reactions performed with substrates possessing electron-rich and halogen groups on the aromatic substituents of the *N*-allylynesulfonamide occurred smoothly generating the corresponding bicyclic products in chemoselectivity. The structure of product **2f** was identified spectroscopically and confirmed by X-ray diffraction analysis. Moderate yield (**2h**, 58%) was obtained from the reaction of ynamide with an electron-withdrawing cyano group at the *para*-position of the aryl substituent. In addition to the *N*-tosylynamides, mesyl-, nosyl-, and *tert*-butyloxycarbonyl-protected substrates were ideal reagents as well, yielding products with high yields (**2i**–**2k**, 84–90%). The scope with respect to the ynamides bearing an allyl unit with different degrees of substitution was then explored. The reaction of the *β*-methallyl tethered substrate delivered the desired bicyclic product **2l** in good yield; product **2m** was isolated in 61% yield from the reaction performed in acetone with gem-dimethylallyl-substituted ynamide. Both *trans*-crotyl and *trans*-cinnamyl tethered ynamides participated in the photoinduced cyclopropanation furnishing products in good yields, 74 and 86% respectively.

We then sought to generalize this photoinduced cyclopropanation to the synthesis of various 3-azabicyclo[4.1.0]heptanes and 3-azabicyclo[5.1.0]octanes. Our initial examination of *N*-3-butenylynamide **4a** was performed under the optimized conditions for *N*-allylynamide (Table 1). To our delight, the desired 3-azabicyclo[4.1.0]heptane **6a** was furnished in 70% yield. Continuing the optimization with *N*-3-butenylynamide **4a** (Table S2, ESI†), we observed an increase in the yield of **6a** (89%) by using 3,6-di-*tert*-butyl-substituted acridinium[12] Mes-(^{t}Bu)$_2$Acr-PhBF$_4$ in place of Mes-Acr-PhBF$_4$ as the photocatalyst. As summarized in Table 2a, a series of 3-azabicyclo[4.1.0]heptanes bearing various arene substituents were successfully produced (**6a**–**6g**, 64–90%) catalyzed by Mes-(^{t}Bu)$_2$Acr-PhBF$_4$. The *N*-3-butenylmeylynamide was a suitable substrate as well,

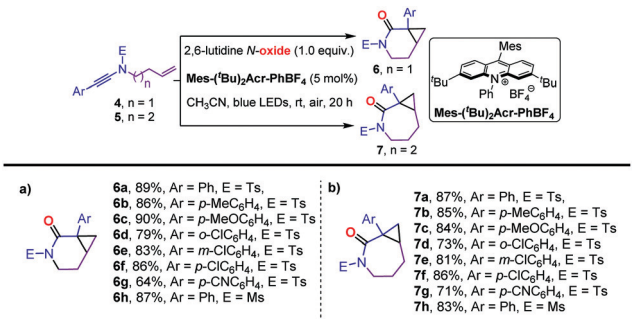
Table 1 Scope of *N*-allylynamides[a]



Entry	Substrate **1**	**2**[b] (%)
1	Ar = Ph, E = Ts, R^1 = R^2 = R^3 = H	**2a**, 88
2	Ar = *p*-MeC$_6$H$_4$, E = Ts, R^1 = R^2 = R^3 = H	**2b**, 90
3[c]	Ar = *p*-MeOC$_6$H$_4$, E = Ts, R^1 = R^2 = R^3 = H	**2c**, 91
4	Ar = *p*-ClC$_6$H$_4$, E = Ts, R^1 = R^2 = R^3 = H	**2d**, 92
5	Ar = *p*-BrC$_6$H$_4$, E = Ts, R^1 = R^2 = R^3 = H	**2e**, 86
6	Ar = *o*-ClC$_6$H$_4$, E = Ts, R^1 = R^2 = R^3 = H	**2f**, 75
7	Ar = *m*-ClC$_6$H$_4$, E = Ts, R^1 = R^2 = R^3 = H	**2g**, 83
8	Ar = *p*-CNC$_6$H$_4$, E = Ts, R^1 = R^2 = R^3 = H	**2h**, 58
9[c]	Ar = Ph, E = Ms, R^1 = R^2 = R^3 = H	**2i**, 90
10	Ar = Ph, E = *p*-Ns, R^1 = R^2 = R^3 = H	**2j**, 84
11	Ar = Ph, E = Boc, R^1 = R^2 = R^3 = H	**2k**, 81
12	Ar = Ph, E = Ts, R^1 = CH$_3$, R^2 = R^3 = H	**2l**, 80
13[d]	Ar = Ph, E = Ts, R^1 = H, R^2 = R^3 = CH$_3$	**2m**, 61
14[e]	Ar = Ph, E = Ts, R^1 = H, R^2 = CH$_3$, R^3 = H	**2n**, 74
15[f]	Ar = Ph, E = Ts, R^1 = H, R^2 = Ph, R^3 = H	**2o**, 86

[a] For experimental details, see ESI. [b] Isolated yield. [c] 10 h. [d] Solvent = acetone. [e] d.r. = 2.7 : 1. [f] d.r. = 17 : 1.

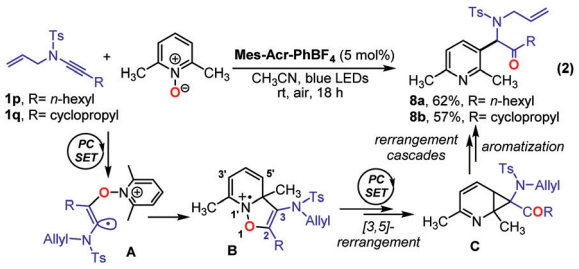
Table 2 Synthesis of 3-azabicyclo[4.1.0]heptanes **6** and 3-azabicyclo[5.1.0]octanes **7**[a]



[a] For experimental details, see ESI.

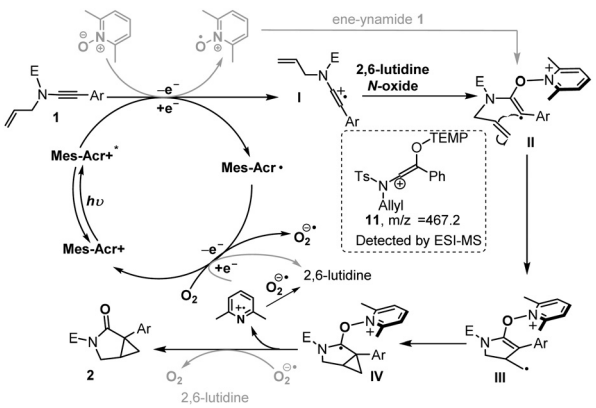
producing **6h** in 87% yield. Moreover, we were pleased to find that 3-azabicyclo[5.1.0]octanes **7** could also be readily accessed from the corresponding *N*-4-pentenylynesulfonamide **5** in good to high yields under the photocatalytic conditions (Table 2b, **7a**–**7h**, 69 to 87%). The structures of **6** and **7** were unambiguously identified spectroscopically and confirmed by X-ray crystallography of **6f** and **7d** respectively. Noteworthily, this photoinduced reaction provides a mild metal-free and conveniently achieved synthesis of valuable azabicyclic compounds, which were only accessible from piperidine/azepane precursors or precious metal catalyzed reactions.

With the successful construction of cyclopropane fused five/six/seven-membered bicycles, we set out to further test the photocatalyzed reaction of *N*-allylynamides with an alkyl substituent at the alkyne terminus. Intriguingly, when *n*-hexyl or cyclopropyl substituted ynamides were subjected to the photocatalytic reaction, unexcepted meta-alkylation products of 2,6-lutidine *N*-oxide with ynamide were obtained albeit in moderate isolated yields (**8a** and **8b**, eqn (2)). The alkyl substituted bicyclic compounds were not detected. We rationalize that the formation of these oxyalkylation products was on account of the switched site-selective generation of vinyl radical intermediate **A**, in which the allyl tethered sulfonamide provided greater resonance stabilization than the alkyl substitution. Such switched selectivity is consistent with our previously reported *ortho*-alkylation of pyridine *N*-oxide with alkyl substituted ynamides.[6] It is proposed that the photocatalytically generated pyridinium vinyl radical **A** could then undergo the Minisci-type transformation affording the bicyclic aminyl radical cation **B**. Recently, the Maulide group reported a *meta*-selective oxyarylation of alkynes with pyridine *N*-oxide.[13] The mechanistic and computational studies of the *meta*-oxyarylation revealed that the reaction proceeded through pseudopericyclic [3,5] rearrangements and a key cyclopropane intermediate. Accordingly, in our *meta*-alkylation we proposed that the cyclopropane intermediate **C** was generated from aminyl radical cation **B** *via* simultaneous or successive-stepped [3,5] rearrangement, N–O bond scission, and a SET process. Subsequent rearrangement cascades driven by aromatization lead to compound **8**.



In further probing the synthetic utility of this photoinduced transformation, we were pleased to find that the photocatalytic reaction of *N*-propargyl ynamide **9a** produced an oxidative cycloisomerization product **10a** in 61% yield, when 2.5 equiv. of 2,6-lutidine *N*-oxide was used (eqn (S1), ESI†). For R = CH_3 (**9b**), besides the generation of 2-oxopyrrolidine **10b**, a diene product **10c** was isolated in 41% yield. It is proposed that the catalytically generated cationic vinyl radical through single-electron oxidation of ynamide and 2,6-lutidine *N*-oxide reacted with the tethered alkyne to afford a new vinyl radical intermediate **D**, which can be oxidized by 2,6-lutidine *N*-oxide to yield product **10**. When R was a methyl group (**9b**), 1,2-hydrogen migration may produce the diene compound **10c**.

To lend further insight into the mechanism of the transformation, mechanistic studies including fluorescence quenching studies, electrochemical studies, and radical inhibition experiments, were performed. Stern–Volmer fluorescence quenching studies (Fig. S3 to S6, ESI†) of the *N*-allylynamide **1a** and 2,6-lutidine *N*-oxide system demonstrated that the light-excited photocatalyst Mes-Acr^{+}* was more significantly quenched by ynamide **1a** (K_{sv} = 80.90) than by 2,6-lutidine *N*-oxide (K_{sv} = 52.29). And the mixed solution of **1a** and 2,6-lutidine *N*-oxide exhibited similar fluorescence quenching efficiency (K_{sv} = 83.85) to the solo *N*-allylynamide **1a** solution, which indicated that the irradiated photocatalyst might be quenched by ynamide **1a** rather than by 2,6-lutidine *N*-oxide. Notably, besides the expected suppression of the photocatalyzed reaction



Scheme 2 Plausible mechanism.

with addition of radical scavenger 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), the formation of **11** from ynamide cation radical **I** and TEMPO was detected by ESI-MS analysis (Scheme 2 and Fig. S1, ESI†). Moreover, *N*-allylynamide **1a** (irreversible half-peak potential, $E^{ox}_{1/2}$ = 1.58 V *vs* SCE) possesses much lower oxidation potential than 2,6-lutidine *N*-oxide does ($E^{ox}_{1/2}$ = 1.82 V *vs* SCE). Based on the aforementioned results, it is more feasible that the generation of ynamide cation radical **I** from photocatalyzed single-electron oxidation of *N*-allylynamide **1a** may initiate this photoinduced transformation. Given the high excited-state reduction potential of catalyst Mes-Acr-PhBF$_4$ ($E^*_{red} = 2.20$ V),[12] the pathway of photoinduced single-electron oxidation of 2,6-lutidine *N*-oxide cannot completely be excluded at this stage.[7]

Herein, in accordance with the experimental evidence and our previous work,[6] a plausible mechanism is proposed in Scheme 2. We hypothesized that the *N*-allylynamide **1** could be formally oxidized by the excited acridinium photocatalyst affording a ynamide cation radical **I**. Subsequent nucleophilic α-addition of the resultant cation radical **I** by 2,6-lutidine *N*-oxide would lead to the formation of the key oxypyridinium tethered vinyl radical intermediate **II**. Alternatively, a photoinduced single-electron oxidation of 2,6-lutidine *N*-oxide is also possible. Nevertheless, subsequent radical addition of ene-ynamide **1** and 2,6-lutidine *N*-oxide radicals would generate the oxypyridinium tethered vinyl radical intermediate **II** as well. Guided by the reported experimental and computational studies of radical ring closure,[14] we propose that the vinyl radical may undergo a 5-*exo*-*trig* radical cyclization with tethered alkene producing intermediate **III**. This open-shell radical is subsequently trapped intramolecularly by the enol frame to close the cyclopropane ring forming a ketyl radical **IV**. The resultant intermediate **IV** could then undergo a β-N–O bond scission yielding the oxygenative cyclopropanation product **2** and 2,6-lutidine radical cation. Based on the literature survey and our experimental results, it is proposed that the acridine radical Mes-Acr could be oxidized by O_2 regenerating acridinium Mes-Acr$^+$ and superoxide O_2^{-}.[12,15] The strongly basic superoxide should readily reduce the 2,6-lutidine radical cation, although the 2,6-lutidine radical cation intermediate might be capable of catalyst turnover. Another putative pathway with direct reduction of ketyl radical **IV** by reactive superoxide and subsequent N–O bond scission may account for the product formation as well.

In summary, we have developed a photoinduced oxidative cyclopropanation of ene-ynamides *via* photocatalytically generated vinyl radical involved radical cascades. The protocol provides a convenient metal-free access to a variety of valuable 3-aza[*n*.1.0]bicycles. Notably, this photocatalytic strategy of cationic vinyl radical generation and the successful radical trapping by the tethered alkene demonstrates its synthetic potential of developing versatile cascade/tandem radical transformations. Further investigation of this transformation and the expansion of this strategy with other radical acceptors to allow the synthesis of molecular complexity are currently underway.

Conflicts of interest

There are no conflicts to declare.

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