Aziridination via Nitrogen-Atom Transfer to Olefins from Photoexcited Azoxy-Triazenes

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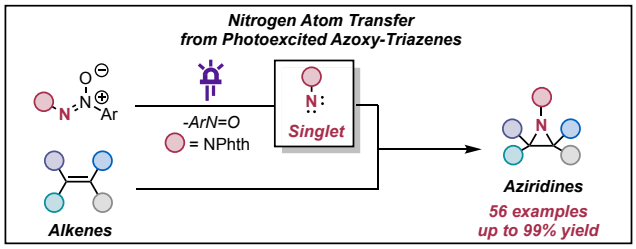
Supporting Information Placeholder

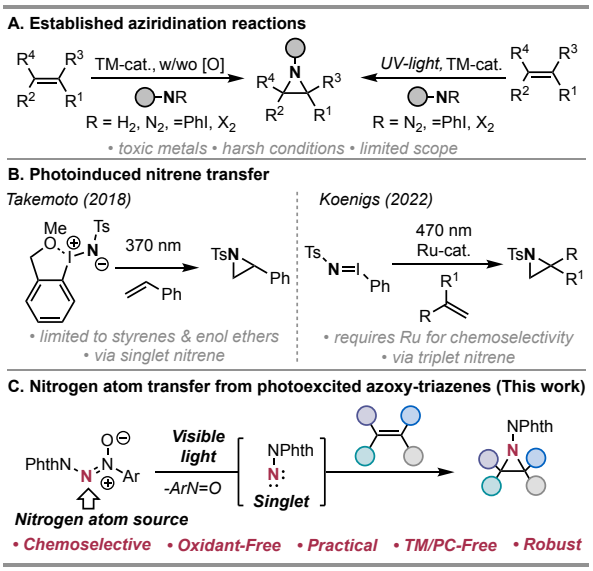


ABSTRACT: Herein, we report that readily accessible azoxy-triazenes can serve as nitrogen atom sources under visible-light excitation for the efficient aziridination of alkenes. This approach eliminates the need for external oxidants, precious transition metals, and photocatalysts, marking a departure from conventional methods. The versatility of this transformation extends to the selective aziridination of both activated and unactivated multi-substituted alkenes of varying electronic profiles. Notably, this process avoids the formation of competing C–H insertion products. The described protocol is operationally simple, scalable, and adaptable to photoflow conditions. Mechanistic studies support that the photofragmentation of azoxy-triazenes results in the generation of a free singlet nitrene that governs the observed chemoselectivity and stereospecificity of the reaction. Our findings contribute to the advancement of sustainable and practical methodologies for the synthesis of nitrogen-containing compounds, showcasing the potential for broader applications in synthetic chemistry.

Aziridines are among the simplest nitrogen-containing heterocycles in organic chemistry.[1,2,3] Their inherent ring strain of 27 kcal mol^{-1} allows them to be potent synthetic handles to access valuable 1,2-aminofunctionalization products, which are featured in natural products and pharmaceutically relevant compounds.[4,5,6,7,8] In some cases, the aziridine core itself plays a significant role in the anti-tumor activity of certain small therapeutics and natural products, like mitomycin.[9] Therefore, innovative strategies to access aziridine motifs continue to be of active interest among the synthetic community. Common strategies include the [2+1] cycloaddition of reactive nitrene intermediates with olefins.[10,11] However, many of these methodologies necessitate the use of transition metal catalysts with activated nitrene precursors such as haloamines, iminoiodinanes, and organic azides, or under oxidative conditions with amines (Scheme 1A, Left).[12,13,14,15,16,17] While each approach offers unique advantages, these methods are conducted under harsh conditions and can suffer from low substrate scope.

Throughout the years, approaches for the photogeneration of nitrenes have evolved, presenting complementary advantages over conventional thermal methods.[18,19] Previously constricted to ultraviolet light and transition metals for intermolecular nitrene transfer (Scheme 1A, Right), recent progress encompasses direct photolysis or the utilization of photocatalysts under mild visible-light conditions for the liberation of free nitrenes.[20] In 2018, the Takemoto group demonstrated that photoexcitation of specialized *ortho*-substituted iminoiodinanes can effectively produce a free singlet nitrene (Scheme 1B, Left),[21] however, this method was restricted to silyl enol ethers and styrenes. In 2022, Koenigs reported that blue light excitation of iminoiodinanes can engender triplet nitrene formation, leading to allylic C–H insertion products. With the addition of a Ru-based photoredox catalyst, the reaction mechanism can be redirected to generate a nitrogen radical anion intermediate that can react with alkenes to produce aziridines, albeit with low stereospecificity (Scheme 1B).[22] Unfortunately, the reliance on precious metals like Ru[23] for chemoselectivity can be seen as a limitation from a cost perspective. Thus, the development of a metal- and oxidant-free aziridination method is highly warranted. Herein, we report that readily synthesized azoxy-triazenes can lead to the formation of free nitrenes under direct visible-light irradiation to enable the stereospecific and chemoselective aziridination of alkenes (Scheme 1C).

Scheme 1. Aziridination of Alkenes.



Previously, our group and others have reported the use of photoexcited nitroarenes as oxygen-atom-transfer agents to access alcohols from hydrocarbons,[24] and carbonyl derivatives from alkenes, aldehydes, and imines.[25,26,27] Hence, we hypothesized

Table 1: Scope of the Photoinduced Azoxy-Triazene Promoted Aziridination Reactions.[a,b]

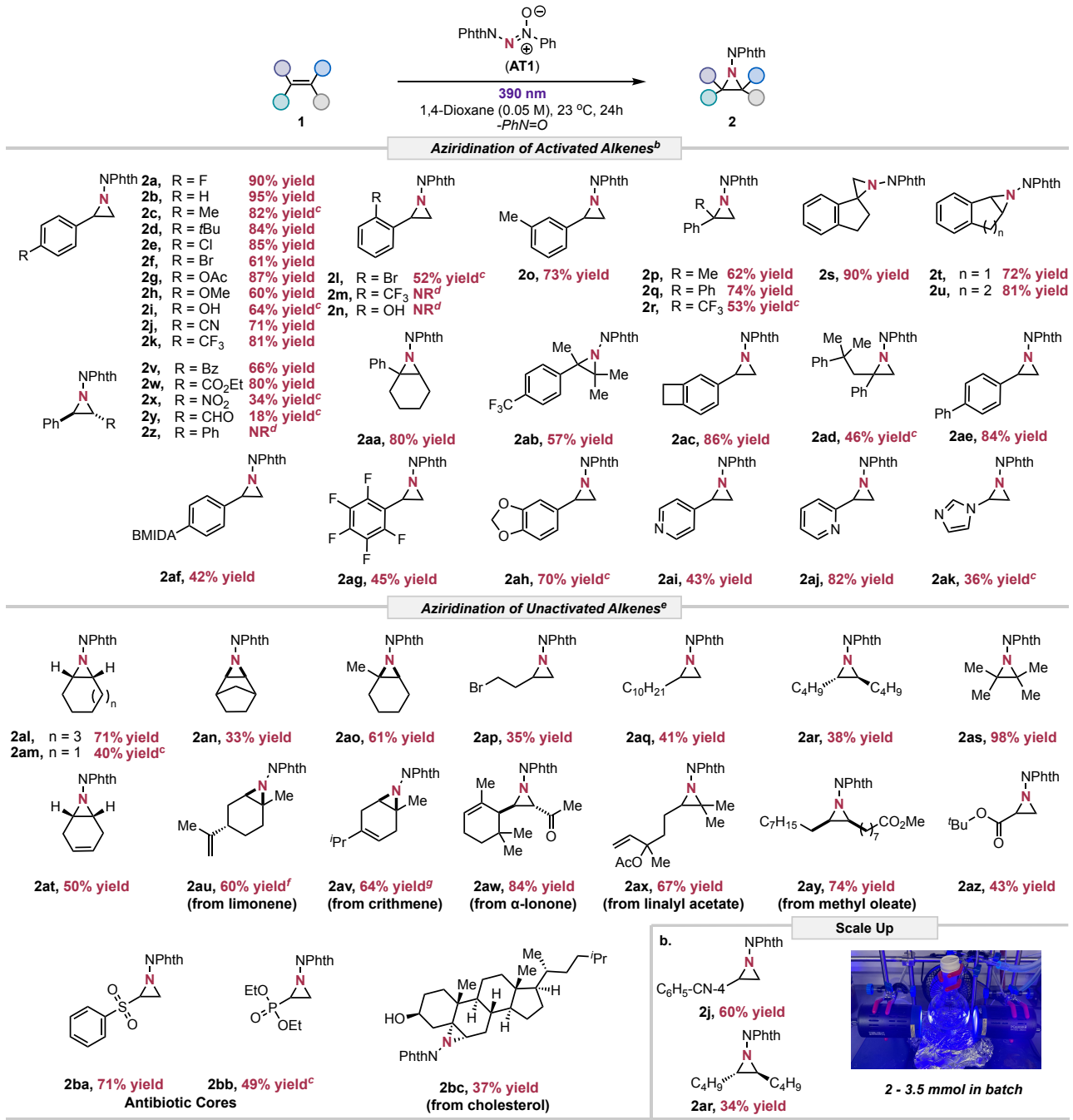


Table 1. [a] Isolated Yields. [b] Conditions: 1-phenyl-2-phthalimidodiazene-1-oxide (1 equiv.), 1.2 equivalents of alkene, 390 nm, 1,4-Dioxane (0.05M), 23 °C, 24h, rt. [c] Denotes ^{1}H NMR yield using CH_2Br_2 as an external standard. [d] No Reaction. [e] Using 2.0 equiv. of alkene; 0.025M. [f] As the major product (d.r. 50:50); 4% ^{1}H NMR yield of minor product (**2au1**, see SI) was detected. [g] As the major product; 14% ^{1}H NMR yield of minor product (**2av1**, see SI) was detected.

the use of isoelectronic azoxyarenes may trigger a nitrogen-atom-transfer event under visible-light irradiation with alkenes to give to aziridines. In 1981, Hoesch and Köppel reported a single example of using azoxyarenes as nitrene precursors under harsh UV-light.[28] In the preparation of this manuscript, the Koenigs group illustrated that tosyl-protected azoxyarenes are capable of undergoing direct visible-light excitation leading to N–S bond homolysis to achieve group transfer of the azoxy to alkenes.[29] Conversely, we postulated that the use of a phthalimide-protected azoxy-triazene, featuring a stronger N–N over an N–S bond, may lead to a nitrogen-atom-transfer of a phthalimide-protected amine under visible-light irradiation for the functionalization of alkenes.

To test our hypothesis, we subjected 4-fluorostyrene (**1a**) and readily synthesized 1-phenyl-2-phthalimidodiazene-1-oxide (**AT1**)[28,30,31] in dichloromethane to 390 nm light irradiation, which resulted in the desired nitrogen-atom-transfer event leading to the aziridine product (**2a**) in 70% ^{1}H NMR yield. Once the optimized reaction conditions were obtained (see SI for details), the electronic effect of the aziridination reaction was investigated with 4-substituted-styrene derivatives (Table 1, **1a–k**). It was found that the transformation was not impacted by the electronic pattern, as substrates possessing both electron-rich and deficient groups resulted in good to high yields (**2a–k**, **2o**, 60-95%). Furthermore, substituents such as –Me (**1c**), –*t*Bu (**1d**), and –OH (**1i**), which are prone to C–H nitrene insertion or hydrogen atom transfer were tolerated in high yields. Next, we investigated disubstituted alkenes under the reaction conditions, which gave moderate to excellent yields (**2p-2x**; **2ad**, 34-90%) of the desired aziridination products. Notably, aziridination of electron-deficient styrene **1r** is challenging under TM-free conditions,[32] however, aziridine **2r** was obtained in 53% ^{1}H NMR yield under our conditions. Among the β-substituted styrenes, cinnamaldehyde (**1y**) gave **2y** in low yield (18%) and cis-stilbene (**1z**) yielded no reaction. The latter outcome is likely due to strong fluorescence quenching of the starting material. Challenging trisubstituted (**1aa**) and tetrasubstituted (**1ab**) styrenes yielded **2aa-ab** in moderate to good yields under the reaction conditions.

Bicyclic-substituted styrene **1ac** generated **2ac** in good yield. Other styrenes like *p*-biphenyl (**1ae**) and sterically encumbered styrene (**1ad**), resulted in 84% of **2ae** and 46% of **2ad**, respectively. Substrate **1af,** possessing a BMIDA functional handle, was tolerated under the reaction conditions (**2af**, 42%).[33] Highly electron-deficient styrenes, such as **1ag,** resulted in a moderate yield of the aziridination product. The highly sensitive acetal group of **1ah**, with a weak C–H bond that is prone to nitrene insertion, led to the aziridination product **2ah** selectively in a good ^{1}H NMR yield (64%). Other substrates prone to fluorescence quenching of **AT1** such as heterocyclic amines (**1ai-l**), yielded aziridine products **2ai-2aj** in moderate to good yields (43-82%). However, imidazole (**1ak**) produced a low yield (**2ak**, 36%).

Next, unactivated olefins were studied under the conditions, (see SI for optimization). Subjecting cycloalkenes to the reaction conditions resulted in good yields of the aziridination products (**2al-am**, 71-85%), whereas bicyclic norbornene gave **2an** in 33% yield. Cyclic trisubstituted olefins possessing a methyl (**1ao**) substituent generated the corresponding aziridine **2ao** in moderate yield (61%). For non-cyclic substrates, terminal and internal alkenes led to moderate to excellent yields of the aziridine products (**2ap-2as**, 35-98%).

The regioselectivity of the transformation was examined on unactivated alkenes. 1,4-Cyclohexadiene (**1at**) yielded only **2at** (50% yield) with no diaziridination detected. Limonene (**1au**), a common terpene with both terminal and internal alkenes, produced aziridination product **2au** with a 15:1 ratio of internal (d.r. 50:50) to terminal alkene. Testing the impact of sterics on the reactivity toward alkenes, essential oil Crithmene (**1aw**)[34] was examined. It was found that aziridination (**2aw**) occurred at the less hindered alkene in a 4.7:1 regioisomeric ratio. Next, odorant α-ionone (**1av**),[35] possessing a trisubstituted cyclic and disubstituted linear alkene, was investigated. Aziridination of the disubstituted linear alkene was the sole product detected (**2av**) in good yield. When linalyl acetate (**1ax**) was tested, boasting both non-cyclic internal and terminal alkenes, regioselective aziridination of the internal alkene was obtained in 67% yield (**2ax**). These regioselectivity studies indicate that the aziridination event is sensitive to the steric profile of alkenes. The cis-fatty acid, methyl oleate (**1ay**), was also tested and gave 74% of **2ay**. Antibiotic cores, **2ba** and **2bb**, were synthesized in good to excellent yields. Finally, complex steroid, such as cholesterol[36] (**1bc**) was subjected to the conditions and gave a moderate yield of **2bc**. Notably, in all cases, allylic C–H amination products were not detected, illustrating that this aziridination approach is highly chemoselective.

To assess the scalability of the method, activated (~1 g of **AT1** with **1j**) and unactivated alkenes (~0.5 g of **AT1** with **1ar**) were used in a batch setup, resulting in comparable yields to our isolation scale in 60% and 34% yields of **2j** and **2ar**, respectively. (Scheme 1B). Employing a photoflow reactor[37,38] (see SI) for substrates with lower yields (**1l**, **1ai**, **1ak**, **1ap**) led to a 3-to-5-fold increase in productivity. Furthermore, derivations of these substrates, such as nucleophilic ring opening of **2m** followed by nickel/hydrazine-promoted N–N cleavage, are possible.[39,40,41,42]

The mechanism of the transformation was then interrogated. UV-Vis indicated that the azoxy-triazene was the sole absorbing species under reaction conditions (Figure S3). Control experiments (Table S4 and Figure S4) established that sustained light exposure was crucial for both the aziridine formation and the fragmentation of the azoxy-triazene. Moreover, experiments involving various triplet-state and singlet-state quenchers indicated that the azoxy-triazene predominantly enters the singlet state upon excitation (Table S6), similar to other azoxyarenes systems.[43,44,45] Since our method results in chemoselective aziridination, singlet nitrene intermediates are likely formed during the reaction progress. To support this, singlet nitrene traps[46,47] such as dimethyl sulfide (DMS, **3a**) and dimethyl sulfoxide (DMSO, **3b**) were used and resulted in trapped products **4a** and **4b** in 20% and >99% ^{1}H NMR yield, respectively (Table 2A), strongly supporting the formation of a singlet nitrene species.

Further support for the formation of the singlet nitrene intermediate can be ascertained by the employment of stereochemical probes,[48,49] where retention of the initial geometry indicates a concerted mechanism via a singlet nitrene, and ablation supports a stepwise mechanism via a triplet nitrene. Geometrically defined unactivated alkenes, (*Z*)-1,4-dichlorobut-2-ene (**5a**) and (*E*)-1,4-dichlorobut-2-ene (**5b**) were subjected to the reaction conditions and resulted in stereospecific aziridination; thus, supporting singlet nitrene formation (Table 2C, Pathway A). However, when activated (*Z*)-β-methylstyrene (**5c**) and (*E*)-α-methylstyrene (**5d**) were investigated, the former resulted in stereoablation of the alkene geometry (2:1, cis to trans), while the latter was stereospecific (1:9, cis to trans) under the reaction conditions (Table 2B). This phenomenon has been reported to occur for β-methylstyrenes with singlet nitrenes.[47,50,51,52] However, this observation could also indicate the possibility of a non-concerted reaction via radical addition of the photoexcited

Table 2. Mechanistic Studies and Proposed Mechanisms.

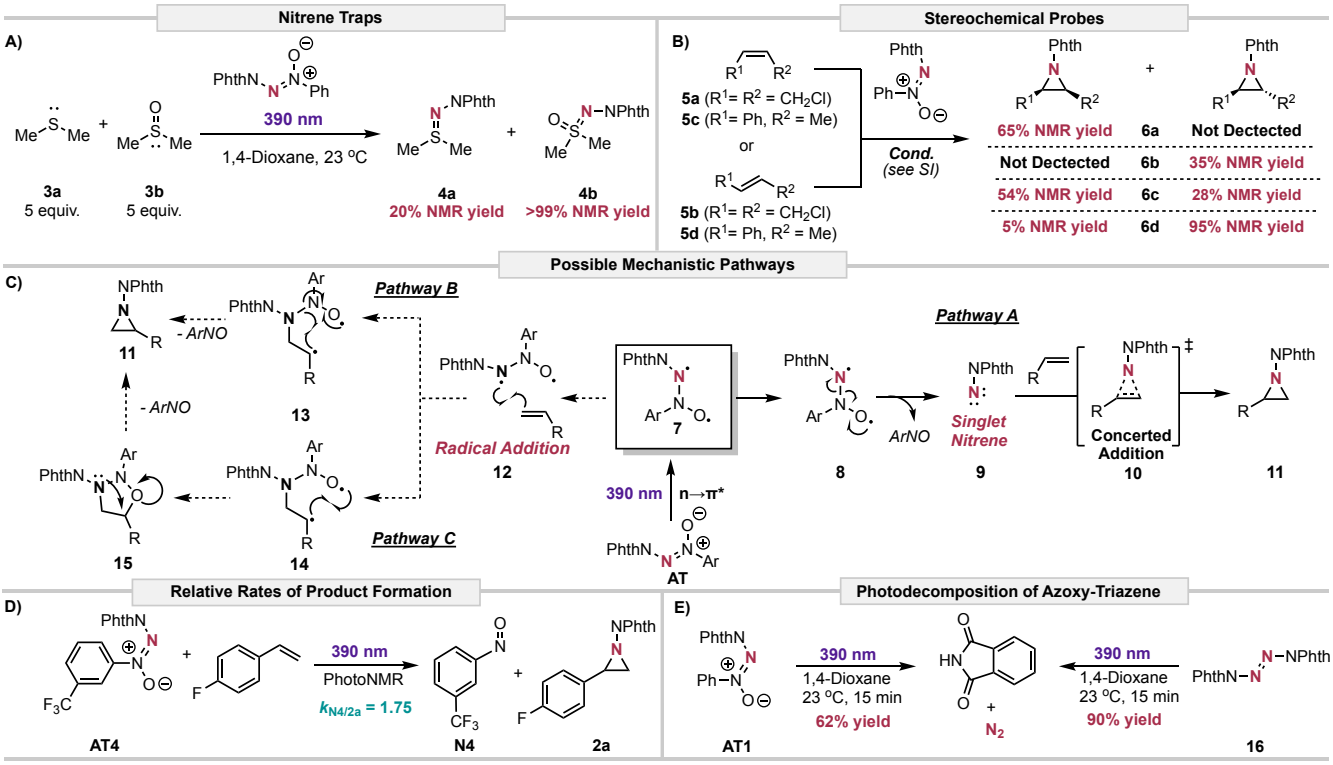


Table 2. A) Nitrene trapping studies. B) Stereochemical probes to determine nitrene identity. C) Possible mechanisms. D) Rates of azoxy-triazene photofragmentation. E) Control study for the photodecomposition of azoxy-triazene.

diradical intermediate **7** to the olefin in a stepwise fashion (**12**) leading to either intermediate **13,** followed by radical fragmentation (Table 2C, Pathway B), or oxadiazolidine intermediate **14** followed by intramolecular fragmentation (**12**→**14**→**15**; Pathway C) to generate the aziridine product.

To determine if aziridination occurs via Pathway A or Pathways B and C, kinetic studies monitoring the growth of the reaction products via ^{19}F-photoNMR were conducted (Table 2D). It was rationalized that the rapid decay of the photoexcited azoxy-triazene (**AT4**) leading to a free nitrene may lead to a higher initial rate of nitroso formation (**N4**) compared to aziridination (**2a**), contrary to a stepwise radical addition which would have proportional growth of nitrosoarene and aziridine. The observed rate slightly favored nitrosobenzene formation over aziridine ($k_{N4/2a}$ = 1.75), indicating the probable generation of a free singlet nitrene via Pathway A. Further evidence for Pathway A was provided by the photoirradiation of the starting azoxy-triazene material without the presence of alkene, which resulted in significant detection of phthalimide (62% isolated yield), presumably via photofragmentation of nitrene dimer 1,4-bis-phthaloyltetrazene[53] (Table 2E, Left). This was verified by subjecting synthesized 1,4-bis-phthaloyltetrazene (**16**) to the reaction conditions, resulting in the formation of the corresponding phthalimide product in 90% yield (Table 2E, Right).

To rule out the possibility of carbon-centered radical intermediates (**13** or **14**), radical quenchers such as TTBP and TEMPO were added to the reaction conditions and exhibited negligible quenching and no trapped products were observed, suggesting radical intermediates did not predominately govern the reaction. Hammett studies employing *para*-substituted styrenes (Figure S6) illustrated a linear dependence with conventional Hammett parameters (concerted, ρ = -0.54) and a non-linear dependence with radical parameters, supporting a concerted aziridination event with the build-up of a partial positive in the transition state.[54]

Based on the results of our mechanistic studies, the following mechanism is proposed (Table 2C, Pathway A). Azoxy-triazene undergoes direct excitation to the singlet state (**7**), which undergoes photodecomposition to release a free singlet nitrene (**9**) and the nitrosoarene byproduct. The singlet nitrene undergoes a concerted [2+1] cycloaddition (**10**) event with olefins to generate aziridines (**11**) with high degrees of stereospecificity and chemoselectivity.

In conclusion, we have illustrated that photoinduced azoxy-triazenes can promote a nitrogen atom transfer event for the chemoselective aziridination of activated and unactivated alkenes. Our method leverages the singlet-excited state of the azoxy-system that is accessed upon visible-light excitation, which subsequently fragments to generate free singlet nitrenes. A wide range of functional groups were tolerated that can be difficult via traditional methods owing to the mild conditions of the transformation. The relatively benign, metal-free method to attain reactive nitrene intermediates at the expense of readily accessible azoxy-triazenes is a distinct feature of this methodology that opens avenues for sustainable aziridination events and related nitrogen atom transfer reactions.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information Statement

The Supporting Information is available free of charge on the ACS publications website. Experimental details, optimization studies, characterization data, and NMR spectra (PDF).

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All authors have approved the final version of the manuscript.

Notes

Any additional relevant notes should be placed here.

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ABBREVIATIONS

NMR, nuclear magnetic resonance; PhotoNMR, photochemical nuclear magnetic resonance; TTBP, 2,4,6-tri-tertbutylphenol; and TEMPO, 2,6,6-Tetramethylpiperidine 1-oxyl.

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