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Synthesis of Quinolines via the Metal-free Visible-Light-Mediated Radical Azidation of Cyclopropenes

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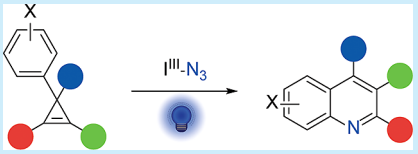
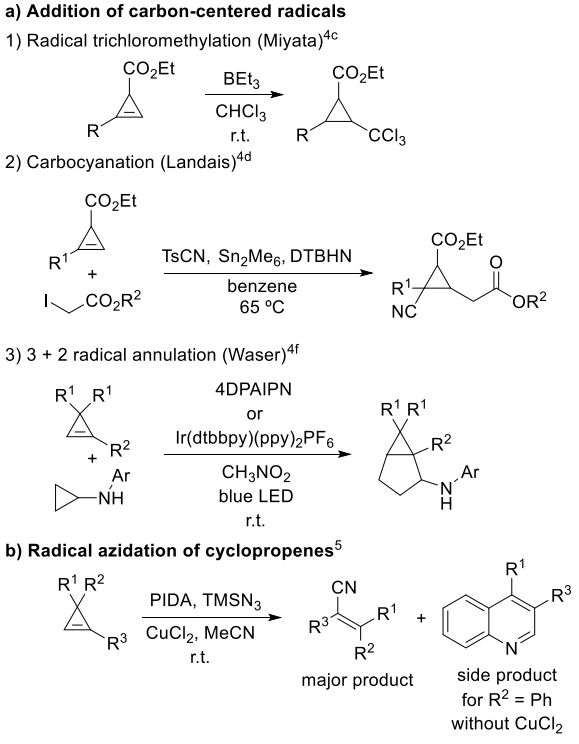
ABSTRACT: We report the synthesis of quinolines using cyclopropenes and an azidobenziodazolone (ABZ) hypervalent iodine reagent as an azide radical source under visible-light irradiation. Multisubstituted quinoline products were obtained in 34−81% yield. The reaction was most efficient for 3-trifluoromethylcyclopropenes, affording valuable 4-trifluoromethylquinolines. The transformation probably proceeds through the cyclization of an iminyl radical formed by the addition of the azide radical on the cyclopropene double bond, followed by ring-opening and fragmentation.



As the smallest cyclic alkenes, cyclopropenes contain a substantial ring strain (ca. 228 kJ mol^{-1}).[1] Nevertheless, cyclopropenes bearing one or two substituents on the aliphatic position are generally stable. Because of the presence of the ring strain, cyclopropenes are useful intermediates in organic synthesis;[2] however, reports of reactions relying on the addition of radicals to cyclopropenes remain scarce, despite the fast growing use of radicals for alkene functionalization (Scheme 1a). The first example of such a reaction was a radical hydrostannylation reported by Nakamura in 1994.[3] Different research groups then reported the addition of carbon-centered radicals to the strained double bond,[4] resulting in hydrotrichloromethylation (eq 1), carbocyanation (eq 2), and 3 + 2 annulation of cyclopropenes (eq 3) among other transformations (Scheme 1a).

In particular, the addition of heteroatom-centered radicals has been mostly neglected. Recently, our group reported the radical azidation of cyclopropenes to give alkenylnitriles (Scheme 1b).[5] During the optimization of this work, small amounts of quinolines were observed as side products for aryl-substituted cyclopropenes, in the absence of $CuCl_2$. Quinolines have found numerous applications in medicine, industry,[6] and material sciences.[7] This heterocycle is present in the structure of many natural products[8] and synthetic bioactive compounds, including examples of approved drugs.[9] For instance, the structures of the antimalarial drugs quinine (**1**) and chloroquine (**2**) and the acetylcholinesterase inhibitor tacrine (**3**) are based on the quinoline core (Scheme 2a). Many classical synthetic methods exist for the synthesis of quinolines, such as the Skraup, Friedlander, Doebner−von Miller, Conrad−Limpach, and Pfitzinger reactions.[10] Most of these methods require acidic or basic conditions, which are not compatible with sensitive functionalities. Therefore, the use of radical-based methods for quinoline synthesis is particularly attractive.[11] A special subclass of such methods are transformations based on cyclizations of iminyl radicals onto the aryl ring.

Scheme 1. Radical-Mediated Transformations of Cyclopropenes



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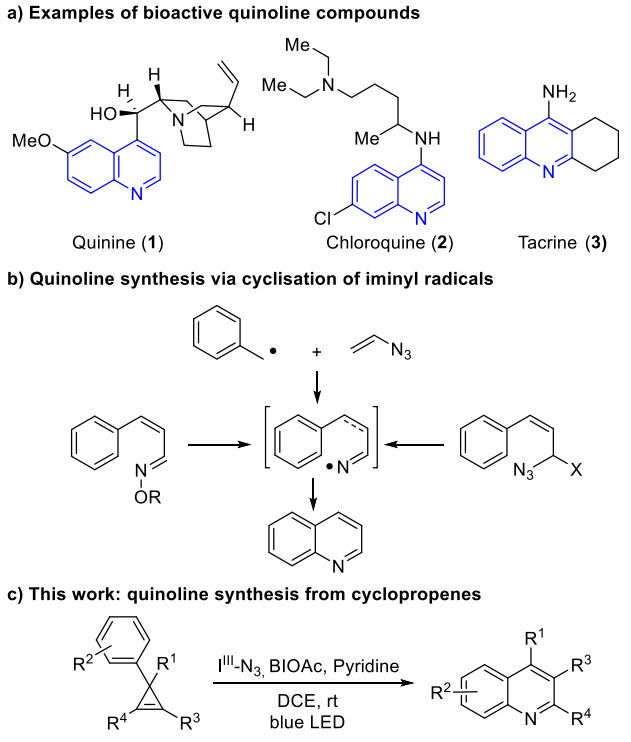
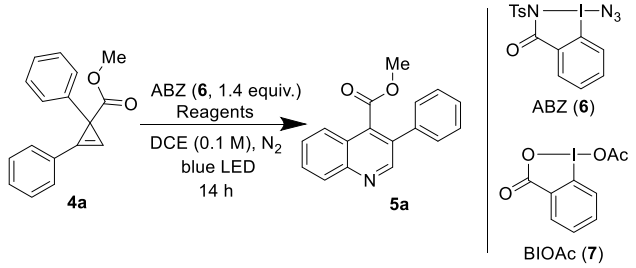
Scheme 2. Quinolines: Bioactive Compounds and Radical-based Synthetic Strategies



These radicals can be accessed via homolysis of the N−O bond in oxime derivatives[12] or by fragmentation of α-azidoradical species (Scheme 2b).[13] Methods to generate the desired iminyl radical remain limited, and new approaches are highly desirable to give access to different substitution patterns. Therefore, we decided to optimize the formation of the quinoline product resulting from the radical azidation of cyclopropenes (Scheme 1b) and report herein a new synthesis of quinolines from cyclopropenes, which is particularly efficient for the synthesis of trifluoromethylated derivatives (Scheme 2c).

Using cyclopropene (**4a**) as the model substrate, we were pleased to find that the use of the safe hypervalent iodine reagent azidobenziodazolone (ABZ, **6**)[14] in the presence of the organic dyes 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)[15] and 1,3-dicyano-2,4,5,6-tetrakis-(diphenylamino)-benzene (4DPAIPN)[16] in 1,2-dichloroethane (DCE) gave the desired quinoline (**5a**) as the single product, albeit in low yield (Table 1, entries 1 and 2). A control experiment revealed that in the absence of a photocatalyst, the reaction proceeded even slightly better (entry 3). No product was observed in the absence of light; however, we found that the reaction outcome was strongly dependent on the batch of ABZ we used, resulting in no product formation in the worst case. We thought that traces of iodine(III) impurities could act as an initiator for the reaction. Indeed, the use of 20 mol % of acetoxybenziodoxolone (BIOAc, 7)[17] as an additive made the reaction reproducible, giving the product in 34% yield (entry 4). No improvement was seen when using 1 equiv of BIOAc (entry 5). The addition of bases to the reaction mixture was examined (entries 6−8), resulting in an improved yield, with pyridine performing the best (entry 8). Despite numerous attempts to increase the reaction yield by fine-tuning the reaction conditions, no improvement could be achieved.

Table 1. Optimization of the Reaction Conditions with Cyclopropene 4a[a]



entry	reagents	yield (%)[b]
1	4CzIPN (5 mol %)	28
2	4DPAIPN (5 mol %)	26
3	none	0−32[c]
4	BIOAc (20 mol %)	34
5	BIOAc (1 equiv)	34
6	BIOAc (20 mol %), K_2HPO_4 (2 equiv)	40
7	BIOAc (20 mol %), 2,6-lutidine (2 equiv)	42
8	BIOAc (20 mol %), pyridine (2 equiv)	44

[a]Reactions were performed on a 0.1 mmol scale. [b]Yield was determined by ^{1}H NMR of the concentrated reaction mixture using CH_2Br_2 as an internal standard. [c]Reaction outcome was dependent on the batch of ABZ.

Because quinoline **5a** was the only product isolable in a substantial amount, we speculate that polymerization of cyclopropene **1a** was occurring as the main side reaction.

Despite the moderate yield obtained for the synthesis of **5a**, we turned to explore the scope of the reaction, as we expected that the reaction efficiency would be highly dependent on the structure of the cyclopropene (Scheme 3). Starting materials were prepared by the metal-catalyzed cyclopropenation of alkynes with diazo compounds using a Rh catalyst for terminal alkynes[18] and a Ag catalyst for internal alkynes.[19] Cyclopropenes **4e−g** were prepared by 1,2-elimination of the corresponding cyclopropyl bromides.[20] We started by evaluating the influence of the substituent at the aliphatic position of the cyclopropene ring. Different ester-substituted cyclopropenes **4a−d** were converted to the corresponding quinoline products **5a−d** in 38−43% yield. For the monosubstituted cyclopropene **4d**, an increased amount of ABZ (**6**) and a prolonged reaction time were required for full conversion. 3-Aryl- (**4e**, **4f**) and 3-alkyl-substituted (**4g**) cyclopropenes were also found to be suitable substrates for the transformation. Aryl-substituted quinolines **5e** and **5f** could be obtained in higher yields (68 and 81%, respectively). To our delight, 3-trifluoromethyl cyclopropene **4h** was converted to quinoline **5h** in 59% yield. The trifluoromethyl group is very popular in medicinal chemistry.[21] Despite the attractiveness of such heterocycles, to the best of our knowledge, there are only two reported examples of the synthesis of 3-aryl, 4-trifluoromethylquinolines without the substituent at position 2 of the heterocyclic ring.[22] Therefore, we focused on the synthesis of trifluoromethyl-substituted quinolines for further exploring the scope of the transformation. Different substituents on the aryl groups in the 1 and 3 positions of the cyclopropenes were tolerated (products **5i−5m**), including electron-rich, electron-poor, and halogen substituents. 1-Alkyl-substituted cyclopropene **4n** gave quinoline **5n** in 34% yield. Interestingly, tetrasubstituted cyclopropenes **4o** and **4p** gave a single regioisomer of quinoline **5o** and **5p**. This method can

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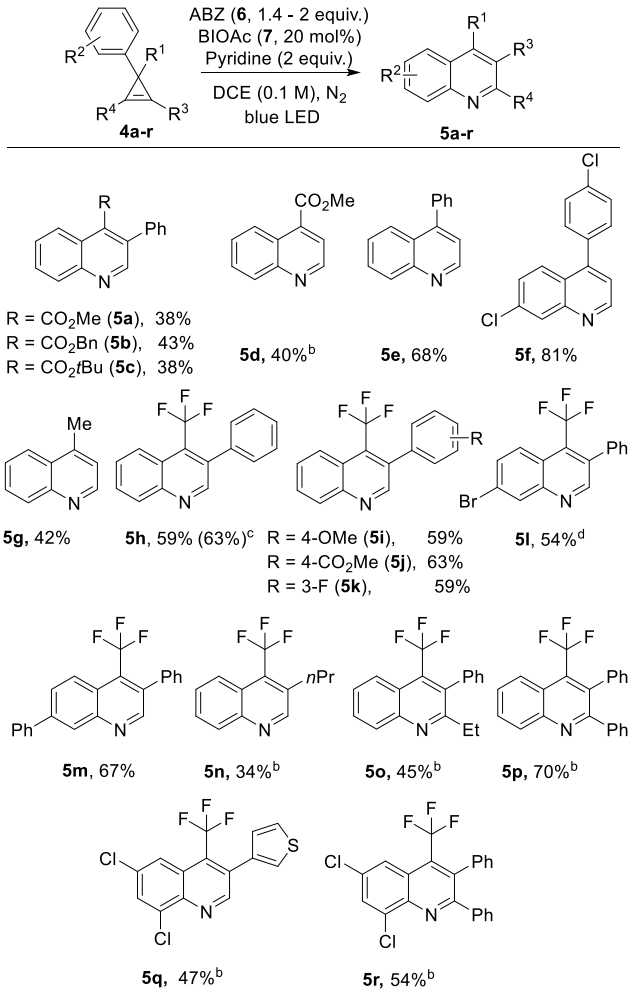
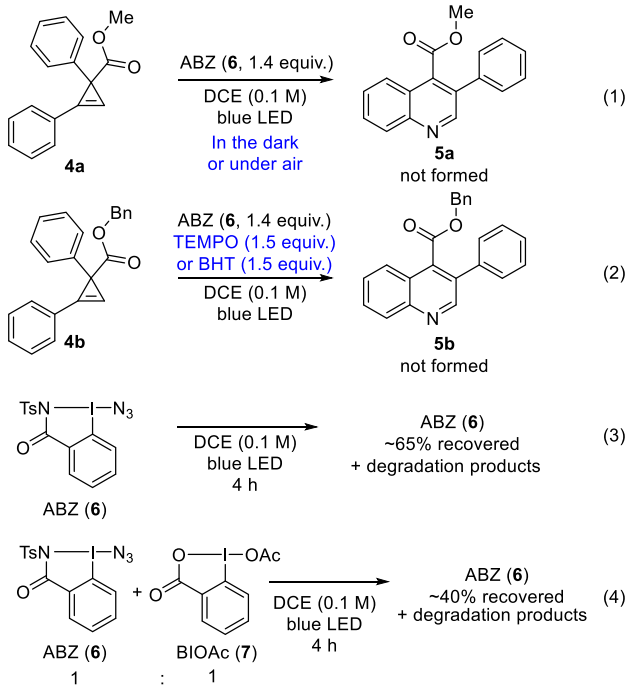
Scheme 3. Substrate Scope[a]

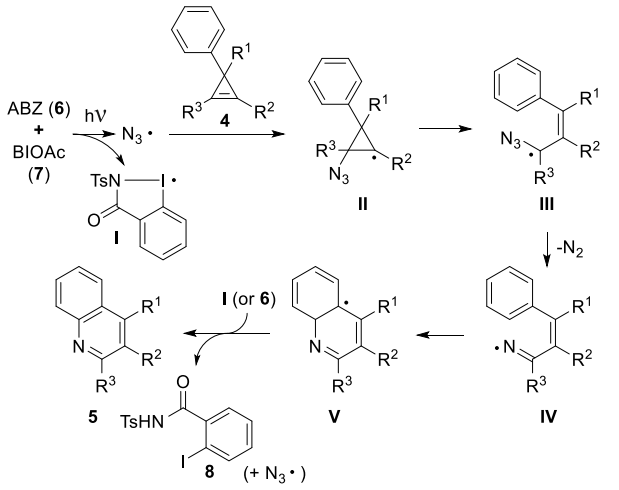


[a]Reaction conditions: 0.2 mmol of cyclopropene, 1.4 equiv of ABZ (**6**), 2 equiv of pyridine, 20 mol % BIOAc (**7**), DCE (0.1 M), room temperature, 14 h. [b]Reaction conditions: 0.2 mmol of cyclopropene, 2 equiv of ABZ (**6**), 2 equiv of pyridine, 20 mol % BIOAc (**7**), DCE (0.1 M), room temperature, 48 h. [c]1.5 mmol scale. [d]0.1 mmol scale.

Scheme 4. Control Experiments



Scheme 5. Mechanism Proposal



also be used for the synthesis of tetra- and pentasubstituted quinolines **5q** and **5r**. 1,2-Dialkylcyclopropenes were found to be inert to reaction conditions, representing a limitation of our methodology. Scale-up of the transformation was straightforward: **5h** was obtained in 63% yield on a 1.5 mmol scale.

Several experiments were then performed to get insight into the reaction mechanism (Scheme 4). It was found that the reaction does not proceed in the dark or under air (eq 1). Performing the reaction in the presence of TEMPO and butylated hydroxytoluene (BHT) as radical scavengers fully inhibits the formation of the product **5b** (eq 2). It was found that ABZ (**6**) slowly degrades under blue LED irradiation (eq 3), whereas the presence of BIOAc significantly accelerates this process (eq 4). Other control experiments showed that cyclopropene **2a** as well as BIOAc (**7**) are stable when irradiated by blue light-emitting diodes (LEDs) as a solution in DCE.

On the basis of these results and our previous investigations,[5] we can suggest the following mechanism for the transformation (Scheme 5). Irradiation of ABZ (**6**) in the presence of BIOAc (**7**) would result in the formation of an excited form, prone to homolytic cleavage of the weak I–N_3 bond, forming an iodanyl radical **I** and an azidyl radical. Once formed, the azidyl radical would add to the cyclopropene double bond, forming the reactive cyclopropyl radical **II**, which would undergo an electrocyclic ring-opening to give the α-azidoallyl radical **III**. α-Azido radicals are known to quickly lose N_2, forming the corresponding iminyl radicals **IV**,[23] which could then cyclize to the adjacent arene ring, giving rise to the intermediate **V**. Subsequent oxidation–deprotonation of **IV** with either iodanyl radical **I** or ABZ (**6**) would result in the formation of product **2** and tosylamide **8**. In the latter case, an azido radical would also be generated, leading to a chain process. The small but reproducible improvement in yield observed in the presence of a base may be due to the acceleration of the deprotonation step or the quenching of the formed acidic species (imide **8** or acetic acid).

In summary, a protocol for the metal-free radical azidation of cyclopropenes leading to the formation of quinolines was

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developed. The hypervalent iodine reagent ABZ (**6**) was used as the source of the azidyl radical under visible-light irradiation. The resulting transformation represents the first method for the synthesis of quinolines via the addition of a radical to a cyclopropene. The overall synthetic strategy is highly convergent, as starting from different alkynes and diazo compounds to access the cyclopropenes, multisubstituted quinolines can be obtained, especially valuable trifluoromethylated heterocycles. Nevertheless, ready access to the required diazo compounds and substitution with functional groups tolerated in cyclopropene ring formation are required for our approach. These results further demonstrate the potential of radical-based reactions with cyclopropenes as useful methods in organic synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01775.

Preparation of starting materials, optimization of reaction, characterization data for products (nuclear magnetic resonance (NMR), infrared (IR), and mass spectrometry (MS)), scale-up and mechanistic studies, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.
Raw data for NMR, IR, and MS are available at zenodo.org: 10.5281/zenodo.4963847.

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