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Visible-Light-Mediated Enantioselective Photoreactions of 3-Alkylquinolones with 4-*O*-Tethered Alkenes and Allenes

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c01065 Read Online

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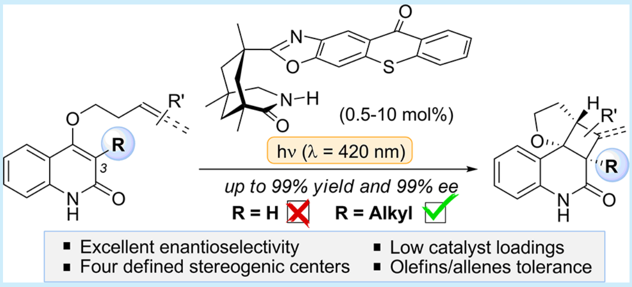
ABSTRACT: The title compounds undergo intramolecular [2 + 2] photocycloaddition reactions when irradiated with visible light in the presence of a chiral sensitizer. Up to four defined stereogenic centers are formed in a single step (14 examples with a tethered alkene, 6 examples with an allene, 72−99% yield, 81−99% ee) at catalyst loadings as low as 0.5 mol %. The alkyl group in the 3-position is crucial for the success of the reaction as it leads to a significant decrease of the triplet energy.



The [2 + 2] photocycloaddition of two olefins has established itself as the most general and most widely used photochemical reaction.[1] Its broad scope and immense versatility render it a valuable transformation for the preparation of substituted cyclobutanes. Up to four stereogenic centers are generated in a single reaction, which in turn poses the challenge to control the relative and absolute product configuration. In this context, the most frequently studied group of substrates are α,β-unsaturated carbonyl compounds, which react readily in solution and allow for an addition to the conjugated double bond.

Despite the significant progress recently made in enantioselective [2 + 2] photocycloaddition chemistry,[2−4] there are still important substrate classes which are synthetically useful but have not yet been studied. In this context, it is striking to note that almost all of the known catalytic processes[4] have been applied to substrates which do not bear an alkyl substituent in the α-position. Indeed, substituents at this position impair coordination to the carbonyl group and may have therefore been avoided.[5] Still, there is a continuing interest in the formation of cyclobutanes with a high degree of substitution, and Figure 1 depicts three representative products, *rac*-**1**,[6] *rac*-**2**,[7] and *rac*-**3**,[8] from the recent literature that were prepared by intramolecular [2 + 2] photocycloaddition reactions. One of the few cyclobutanes obtained in enantiomercally enriched form from an α-substituted enone is dihydroquinolone **4**. The compound was obtained after dynamic crystalline salt formation with a chiral acid, [2 + 2] photocycloaddition with α-methylacrylonitrile, and subsequent base treatment (99% yield, 92% ee).[3c]

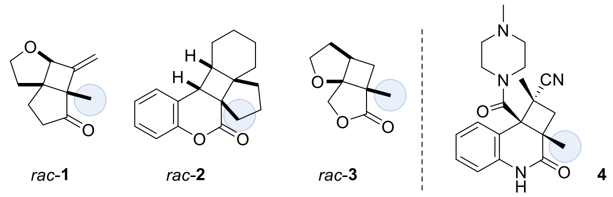


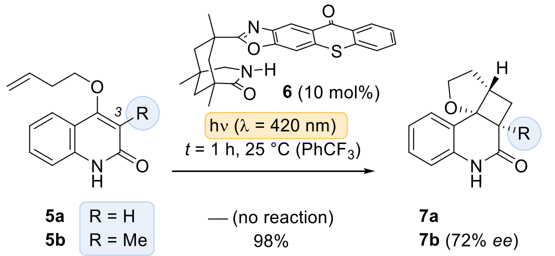
Figure 1. Cyclobutanes *rac*-**1**, *rac*-**2**, and *rac*-**3** originating from α-alkyl-substituted enone substrates and enantioenriched [2 + 2] photocycloaddition product **4**.

In the present study, we have investigated the reaction of various 3-alkyl-substitited quinolones, which bear an alkene or allene unit attached to carbon atom C4 via an alkoxy linker. It was found that the substrates undergo sensitized photochemical reactions employing visible light irradiation (λ = 420 nm). Enantioface differentiation was achieved via a chiral thioxanthone derivative with a lactam hydrogen bonding site.

The triplet state of quinolones is accessible by direct irradiation followed by intersystem crossing (ISC)[9] or by triplet sensitization.[4a,c,10] In the latter case, a photoactive compound with a high triplet quantum yield and with a sufficiently high triplet energy (E_T) is employed to promote the transition of the molecule from the ground state to the triplet state. We have found in previous work that 4-(ω-alkenyloxy)quinolones have a triplet energy that exceeds 270 kJ/mol. Their sensitized intramolecular [2 + 2] photocycloaddition reaction (λ = 366 nm) required the use of a chiral xanthone catalyst (E_T = 316 kJ/mol, 77 K, pentane/isopentane).[2a] An attempted reaction of olefin **5a** (λ = 420 nm) failed in the presence of chiral thioxanthone catalyst **6**[11] (Scheme 1), which also operates by

Received: March 25, 2020

Scheme 1. Sensitized Intramolecular [2 + 2] Photocycloaddition of Quinolone **5a** (R = H) and the Respective 3-Methyl-Substituted Derivative **5b** (R = Me)



hydrogen bonding and which exhibits a lower triplet energy (E_T = 263 kJ/mol, 77 K, trifluorotoluene).[2a] In line with these results, we determined the triplet energy of quinolone **5a** from its phosphorescence spectrum (Figure 2, left) as E_T = 298 kJ/mol (77 K, ethanol). The compound is fluorescent in solution, and the energy of the first excited singlet state was determined from the intercept of the absorption and emission spectrum as 356 kJ/mol (see the Supporting Information (SI) for further details). Remarkably, the α-methyl-substituted analogue of compound **5a**, quinolone **5b**, exhibited a significantly lower triplet energy. Despite the fact that its S_1 transition is shifted only slightly to longer wavelength, the triplet energy was lower by 25 kJ/mol (E_T = 273 kJ/mol, 77 K, ethanol; Figure 2, right). To our delight, we noted that the sensitization of the desired [2 + 2] photocycloaddition of 4-(but-3-enyloxy)-3-methylquinolone by chiral thioxanthone **6** was feasible, and product **7b** was obtained in 98% yield (Scheme 1). Fluorescent lamps served as light sources for the emission, which has a notable spectral overlap with the absorption spectrum of the sensitizer. The reaction was performed at ambient temperature in trifluorotoluene, and the enantioselectivity was moderate (72% ee).

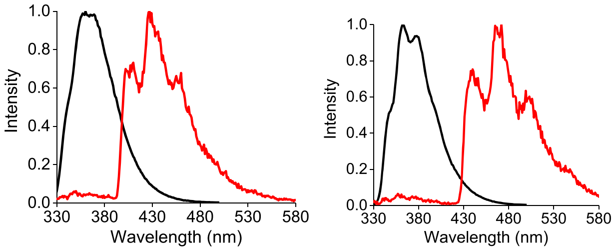
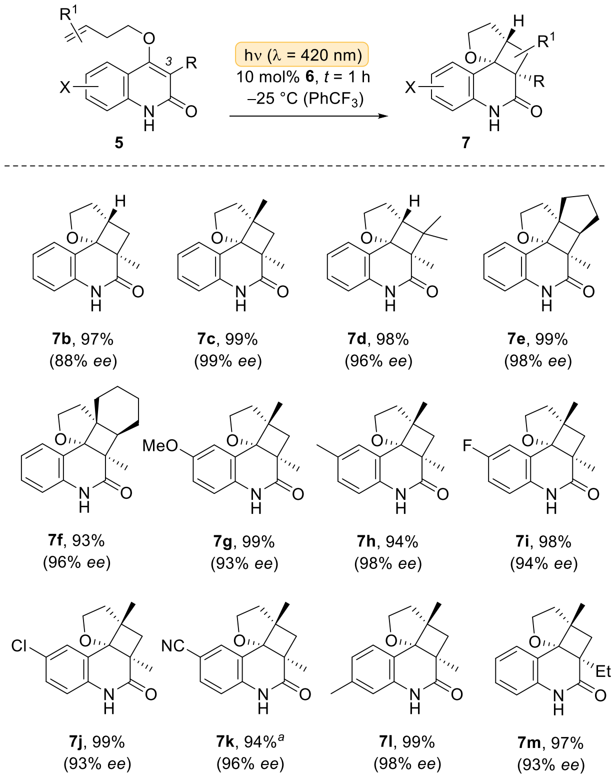


Figure 2. Fluorescence (black) and phosphorescence (red) spectra recorded at rt (fluorescence) and 77 K (phosphorescence) for 4-(but-3-enyl)quinolones **5a** (left) and **5b** (right) in ethanol (for further details, see the SI).

As hydrogen bonding of substrate **5b** and catalyst **6** is a prerequisite for enantioface differentiation (vide infra), any parameter that increases the association constant increases in parallel the enantioselectivity. In this context, trifluorotoluene has been established[4a,c,11] as an ideal nonpolar solvent, which not only enforces the hydrogen bonding interaction but also allows—due its low melting point—the reaction temperature to be lowered. When performing the reaction **5b** → **7b** at −25 °C under otherwise identical conditions, the enantioselectivity was increased to 88% ee (Scheme 2) without compromising the yield (97%). Under these conditions, an array of substituted 3-methylquinolones was subjected to an enantioselective intramolecular [2 + 2] photocycloaddition.

Scheme 2. Intramolecular Enantioselective [2 + 2] Photocycloaddition of 3-Alkyl-4-alkenyloxyquinolones **5** to Cyclobutanes **7**: Reaction Scope



[a]The reaction was performed at a concentration of c = 1.5 mM, with an irradiation time of 1.5 h.

A particular emphasis was put on the construction of sterically congested, highly substituted cyclobutanes (products **7c**–**7f**). Variation of the substituents within the benzo ring of the quinolone skeleton (products **7g**–**7l**) served to demonstrate the functional group tolerance of the enantioselective [2 + 2] photocycloaddition with a methyl, chloro, cyano, methoxy, and fluoro group (94–99% yield, 93–98% ee). Finally, the 3-substituent in the quinolone was altered from a methyl to an ethyl group, which resulted in a slightly lower, but still satisfactory, enantioselectivity (93% ee) recorded for product **7m**.

The absolute configuration of product **7j** could be determined by single-crystal X-ray diffraction (Figure 3), and the assignment of the absolute configuration for the other products is based on analogy. As mentioned above, hydrogen bonding of 1,5,7-trimethyl-3-azabicyclo[3.3.1]nonan-2-ones to lactams is a common motif employed in enantioselective photochemical reactions.[2a] The structure of the putative 1:1 complex of

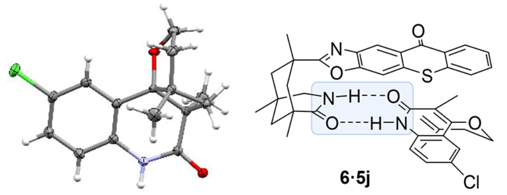
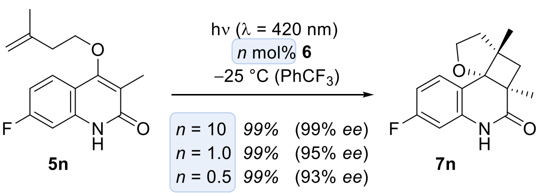


Figure 3. Absolute configuration of product **7j** as determined by anomalous X-ray diffraction (left) and proposed enantioface differentiation within complex **6·5j** (right).

substrate **5j** to catalyst **6** illustrates the suggested binding situation. Direct excitation of quinolones **5** is impossible with the chosen light source due to the absence of any absorbance at $\lambda > 360$ nm. The substrates require an energy transfer from the thioxanthone to engage in a consecutive [2 + 2] photocycloaddition. Upon excitation of thioxanthone **6**, the population of its triplet state occurs within picoseconds,[12] and the close proximity to the quinolone facilitates a rapid energy transfer. The quinolone triplet, in turn, undergoes C−C bond formation by addition to the internal carbon atom of the olefin to a 1,4-diradical, which after ISC generates the product. A high enantioface differentiation is guaranteed as the top face of the quinolone is shielded by the thioxanthone chromophore.

Recently, the use of ruthenium and iridium complexes has been advertised as an alternative to organic triplet sensitizers.[13] The disadvantage of their high molecular weight (MW > 500 Da) is compensated by the fact that they can be used in low quantities (<2 mol %) and that they exhibit high photostability. The present intramolecular [2 + 2] photocycloaddition of quinolones appeared as a suitable reaction to evaluate the photostability and efficiency of catalyst **6**. Quinolone **5n** was chosen as the test substrate (Scheme 3).

Scheme 3. Enantioselective [2 + 2] Photocycloaddition of Substrate 5n to Cyclobutane 7n: Efficiency of Sensitizer 6 at Low Catalyst Loadings

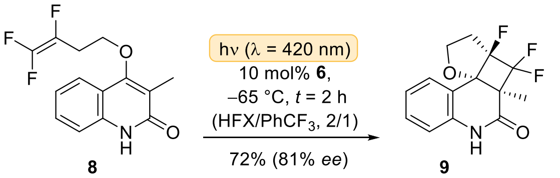


n = 10	*99%*	(99% *ee*)
n = 1.0	*99%*	(95% *ee*)
n = 0.5	*99%*	(93% *ee*)

Under standard conditions with 10 mol % of catalyst **6**, its [2 + 2] photocycloaddition to product **7n** proceeded in 99% yield (99% ee). Lowering the catalyst loading to 1.0 mol % led to a minimal decrease in enantioselectivity, and even at a catalyst loading of 0.5 mol %, the yield and the enantioselectivity remained high. Turnover numbers achieved with catalyst **6** thus exceed 200, and given its low molecular weight (MW = 432.5 Da), minimal quantities are sufficient not only to facilitate a visible-light-mediated reaction but also to maintain a high enantioselectivity.

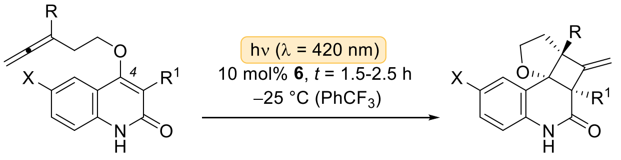
The electronic limits of the alkene part involved in the catalytic intramolecular [2 + 2] photocycloaddition were probed by employing electron-deficient 4-(3,4,4-trifluorobut-3-enyloxy)-3-methylquinolone (**8**) (Scheme 4). Trifluorinated olefins have, to the best of our knowledge, not yet been employed in visible-light-mediated [2 + 2] photocycloaddition reactions.[14] It was therefore gratifying to note that a successful photocycloaddition could be initiated by catalyst **6** at $\lambda = 420$ nm even at low temperature and that product **9** was obtained in 72% yield with significant enantioselectivity (81% ee).

Scheme 4. Intramolecular [2 + 2] Photocycloaddition of Electron-Deficient 4-(3,4,4-Trifluorobut-3-enyloxy)-3-methylquinolone (8) (HFX: Hexafluoro-*m*-xylene)



In two additional sets of experiments, allenes were studied as potential reaction partners in the enantioselective [2 + 2] photocycloaddition. Despite the high synthetic utility of allene photocycloaddition products,[15] this substrate class has received little attention in the context of enantioselective photochemistry.[16] The first set of allenes (compounds **10**) was linked via an ethylene tether to the oxygen atom at carbon C4 of the quinolone. The time required to achieve full conversion in their reaction varied slightly, but in all cases, the desired products **11** were obtained in high yields and with excellent enantioselectivity (Scheme 5). A single regioisomer was obtained with an exocyclic double bond that invites further functionalization.

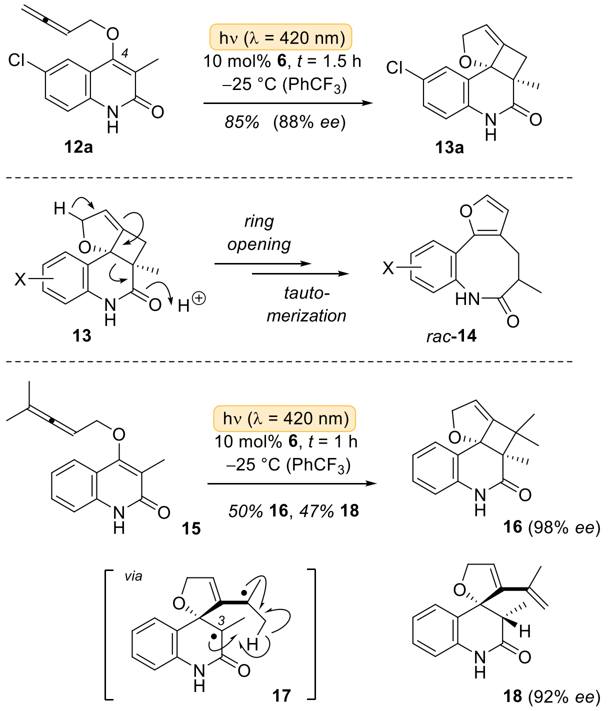
Scheme 5. Enantioselective Intramolecular [2 + 2] Photocycloaddition of 3-Alkyl-4-(penta-3,4-dienyloxy)-quinolones 10



10a	R = H	X = H	R^1 = Me	*85%*	**11a**	(91% *ee*)
10b	R = Me	X = H	R^1 = Me	*98%*	**11b**	(96% *ee*)
10c	R = Me	X = Cl	R^1 = Me	*97%*	**11c**	(91% *ee*)
10d	R = Me	X = H	R^1 = Et	*90%*	**11d**	(92% *ee*)

Quinolones **12**, in which an unsubstituted allene was linked only by a methylene linker to the oxygen atom, reacted also with high regio- and chemoselectivity to a single product. The addition product **13a** of 6-chloroquinolone **12a** could be readily isolated and fully characterized (Scheme 6). The addition occurs in this instance to the terminal double bond of the allene, and the remaining double bond is embedded into a dihydrofuran ring as part of a 4,5,5a-trihydrocyclobuta-2*H*-furan core. The strained enol ether is prone to ring opening, and the photocycloaddition products of other allenes **12** turned out to be less stable than product **13a**. Traces of acid (e.g., 0.5 mol % of H_2SO_4) led to ring opening, which is presumably initiated by protonation at the quinolone C2 oxygen atom (structure **13**).[17] Fragmentation of the cyclobutane ring leaves a positive charge in the allylic position, which is released by deprotonation to form a furan ring. As the fragmentation occurs via a ketene hemiaminal, which subsequently tautomerizes, the only remaining stereogenic center within the newly formed azocinone ring does not retain its configuration, and products **14** were racemic. One of the fragmentation products (X = H) was isolated and fully characterized (see the SI for further details). Terminal dimethyl substitution at the allene revealed that a second enantioselective reaction pathway is accessible beyond the [2 + 2] photocycloaddition. Upon irradiation of substrate **15** in the presence of catalyst **6**, cyclobutane **16** was formed in 50% yield with high enantioselectivity (98% ee). In addition, the formation of diene **18** was observed,[18] and the latter compound was isolated in 47% yield. It seems likely that the product stems from the same 1,4-diradical precursor **17** as cyclobutane **16**. The additional methyl groups open an alternative reaction pathway to intermediate **17**, allowing for intramolecular hydrogen abstraction[19] from the radical at atom C3 of the quinolone ring. The first C−C bond formation step within the complex of compound **15** to sensitizer

Scheme 6. Enantioselective [2 + 2] Photocycloaddition of 4-(Buta-2,3-dienyloxy)-3-methylquinolones 12 and 15: Consecutive Ring Opening and a Competing Reaction Pathway



6 is responsible for the enantioselectivity of the process, and the enantiomeric excess recorded for spiro compound **18** (92% ee) is similar to that of cyclobutane **16**.

In summary, the intramolecular [2 + 2] photocycloaddition of 3-alkylquinolones with 4-*O*-tethered alkenes and allenes has been found to proceed with high enantioselectivity if performed in the presence of a chiral sensitizer. The alkyl substituent in the α-position to the carbonyl group does not impair the binding to the catalyst but rather leads to a significant decrease in the triplet energy ($\Delta E_T \approx 25$ kJ/mol) as compared to that with unsubstituted quinolones. This effect is beneficial because it allows the reaction to be performed in the presence of thioxanthone **6**, which operates with visible light ($\lambda > 380$ nm). Allenes have for the first time been used as reaction partners in the enantioselective [2 + 2] photocycloaddition reaction of quinolones, and they provide intriguing products such as cyclobutanes **11**, **13a**, and **16**. An alternative enantioselective reaction pathway was discovered, which led to spirocyclic product **18** (92% ee).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01065.

> Synthetic procedures and full characterization for all starting materials and products (**5**, **7**−**16**, and **18**), spectroscopic data, NMR spectra, and luminescence studies (PDF)

Accession Codes

CCDC 1988524 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft (Reinhart Koselleck program; GRK 1626) is gratefully acknowledged. X.L. thanks the Alexander von Humboldt foundation for a research fellowship. O. Ackermann, F. Pecho, and J. Kudermann (all TU München) are acknowledged for their help with HPLC and GLC analyses. We are grateful to Dr. A. Bauer and J. Großkopf (all TU München) for recording the luminescence spectra.

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