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[6π] Photocyclization to *cis*-Hexahydrocarbazol-4-ones: Substrate Modification, Mechanism, and Scope

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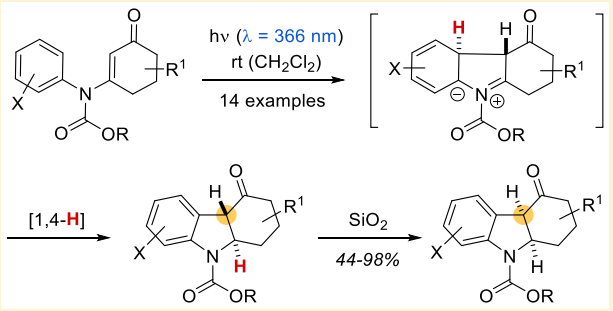
Supporting Information

ABSTRACT: Upon irradiation at λ = 366 nm, tertiary *N*-alkoxycarbonyl-*N*-aryl-β-enaminones furnished exclusively the *trans*-hexahydrocarbazol-4-ones by a conrotatory [6π] photocyclization but epimerized on silica to *cis*-hexahydrocarbazol-4-ones (14 examples, 44−98% yield). The acceptor substitution on the nitrogen atom enhanced the stability of the cyclized products compared to *N*-alkyl-*N*-aryl-β-enaminones reported previously. The mechanism of the [6π] photocyclization was investigated by quenching experiments, deuterium-labeling experiments, and DFT calculations, suggesting a triplet pathway for the conrotatory ring closure followed by a suprafacial [1,4] hydrogen migration.



INTRODUCTION

Photochemical organic transformations provide easy access to molecular structures that are difficult, if not impossible, to obtain via conventional reactions. Numerous approaches toward natural product synthesis have been reported where a photochemical transformation represents a key step.[1] Indoline derivatives are a very important class of heterocyclic compounds due to their presence as core structures in many naturally occurring alkaloids and pharmaceutical compounds.[2] In pioneering work, Chapman and co-workers[3] demonstrated that *N*-alkyl-*N*-aryl-enamines produce upon irradiation mainly *trans*-fused hexahydrocarbazoles, while Schultz et al.[4] reported the formation of *cis*-fused dihydrobenzofurans from β-aryloxyenones via photochemical conrotatory ring closure followed by epimerization. These and other reports proved the efficiency of a [6π] photocyclization reaction in the generation of complex carbo- and heterocycles from simple starting materials.[5,6] In 1988, Gramain, Husson, and co-workers reported the synthesis of *cis*-hexahydrocarbazol-4-ones from tertiary *N*-alkyl-*N*-aryl-β-enaminones by [6π] photocyclization and subsequent base-mediated epimerization (Scheme 1, PMB = *p*-methoxybenzyl).[7] The presence of a carbonyl functional group in the photoproduct allowed for further transformations to various *cis*-hexahydrocarbazol-4-ones and pentacyclic alkaloid skeletons.[8] It is worth noting that despite the importance of these *cis*-hexahydrocarbazol-4-ones as precursors to pentacyclic alkaloid skeletons, a mechanistic study has not been carried out nor have detailed analytical data for *trans*- and *cis*-hexahydrocarbazol-4-ones been reported. This is most probably due to the instability of *trans*- and *cis*-products (**2** and **3**, Scheme 1) at room temperature. Our interest in the photochemistry of enones[9] led us to investigate this classical photoreaction. Apart from the fact that we aimed to isolate and characterize the hexahydrocarbazol-4-one products, we were interested to see whether the enaminones would be amenable toward a chromophore activation[9b] by a Lewis acid.

Enone substrates generally demonstrate a strong bathochromic shift in absorption upon coordination with a Lewis acid,[9] but enaminone **1a** (R = Me) exhibited a bathochromic shift of only Δλ = 10 nm (see Figure S1), suggesting a coordination of the Lewis acid at the nitrogen instead of the enone oxygen atom. Indeed, no conversion was observed upon irradiation of **1a** in the presence of 0.5 equiv of $EtAlCl_2$, indicating that the lone pair of nitrogen that is necessary for the [6π] photocyclization was no longer available. This observation led to the idea to introduce an electron-withdrawing group at the nitrogen atom. After some experimentation, we found that a methoxycarbonyl-substituted enaminone demonstrated a strong bathochromic shift in the presence of Lewis acid (see Figure S2). This observation triggered a more extensive study of the [6π] photocyclization of *N*-alkoxycarbonyl-*N*-aryl-β-enaminones which is reported here in detail.

RESULTS AND DISCUSSION

Reaction Conditions and Scope. Upon irradiation at a wavelength of λ = 366 nm in degassed dichloromethane under

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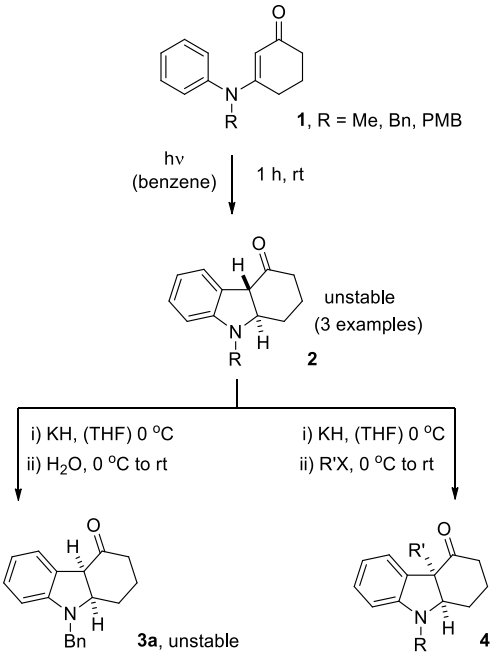
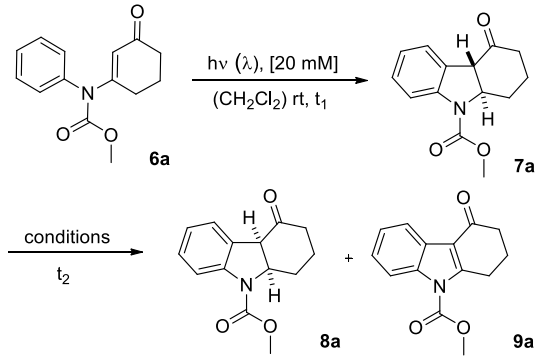
Scheme 1. [6π] Photocyclization of *N*-Alkyl-*N*-aryl-*β*-enaminones 1 and Further Transformations of Primary Products 2 As Reported by Gramain et al.[7]



argon, enaminone **6a** was completely converted to a single product in 3 h, but surprisingly, the product turned out to be the *cis*-hexahydrocarbazol-4-one (Table 1, entry 1, 98% yield). ^{1}H NMR spectral data of the crude reaction mixture established the exclusive formation of *trans*-hexahydrocarbazol-4-one **7a** upon irradiation but complete conversion to the thermodynamically stable *cis*-hexahydrocarbazol-4-one **8a** took place, presumably by epimerization on silica. The relative configuration of **8a** was confirmed by single-crystal X-ray diffraction (see the Supporting Information). It is worth noting that in Gramain's work[7,8] a base-mediated epimerization was necessary to convert the *trans* to the *cis* isomer (Scheme 1), while in our case the epimerization occurred under much milder conditions. In addition, *cis*-product **8a** is a bench-stable white solid compound, proving that the introduction of an acceptor substitution on the nitrogen atom leads to more stable hexahydrocarbazol-4-ones. With this result in hand, we used enaminone **6a** as the standard substrate to perform further irradiation and epimerization experiments. Irradiation at 350 nm gave a result similar to that described above, while at 419 nm no conversion was observed (Table 1, entries 2 and 3). A longer irradiation time of 20 h at λ = 366 nm led to the formation of tetrahydrocarbazol-4-one **9a**, suggesting that *trans*-isomer **7a** was not stable under irradiation and underwent oxidation. Compound **9a** exhibits a higher molar absorption coefficient at λ = 366 nm (ε_{366} = 40 M^{-1} cm^{-1}) than **7a** (ε_{366} = 6 M^{-1} cm^{-1}), and once it is present at a certain concentration it does not allow for further photooxidation of **7a** (Table 1, entry 4). Stirring the *trans* isomer in the presence of silica for 1 h furnished complete epimerization, while interestingly, no epimerization took place in the presence of acetic acid (2 equiv) after 16 h at room temperature (Table 1, entries 5 and 6). Trifluoroacetic acid proved more effective as 2 equiv was sufficient for complete epimerization in 3 h at room temperature (Table 1, entry 7). Stirring the *trans* photoproduct in the presence of 10 equiv of deuterated

Table 1. Reaction Optimization with *N*-Methoxycarbonyl-*N*-phenyl-*β*-enaminone 6a[a]



entry	λ (nm)	t_1 (h)	conditions	t_2 (h)	ratio **8a**/**7a**
1	366	3	on silica[b]		98[c]/0
2	350	2	on silica[b]		95[c]/0
3	419	20			0/0
4	366	20	on silica[b]		74[c]/0[d]
5	366	3	on silica[e]	1	100/0
6	366	3	AcOH (2 equiv)	16	0/100
7	366	3	TFA (2 equiv)	3	100/0
8	366	3	TFA-d_1 (10 equiv)	3	100/0[f]

[a]For the emission spectra of the light sources, see ref 10. Reactions carried out on a 0.2 mmol scale of **6a** using a Duran phototube. The ratio of **8a**/**7a** was determined by ^{1}H NMR integration. [b]Epimerization occurred on silica during column chromatography. [c]Yield of isolated product **8a**. [d]Byproduct **9a** isolated in 12% yield. [e]After irradiation, the reaction mixture was transferred to a round-bottom flask and stirred over silica (2 g). [f]Ratio of deuterium to hydrogen 7:3 at position α to carbonyl. AcOH = acetic acid, TFA = trifluoroacetic acid, TFA-d_1 = monodeuterated TFA.

trifluoroacetic acid produced *cis* compound **8a** with a deuterium to hydrogen ratio of 7:3 at the position α to carbonyl (Table 1, entry 8).

Having the optimized conditions in hand for the photocyclization, we synthesized various tertiary aryl enaminones. The preparation of these enaminones was straightforward and relied on a two-step sequence in which different anilines were coupled with cyclic 1,3-diones using Yb(OTf)$_3$ (2 mol %) as the catalyst to obtain *N*-aryl-*β*-enaminones **5** in the first step.[11]

In the second step, compounds **5** were either deprotonated by *n*BuLi followed by addition of chloroformates (procedure A, for compounds **6a**−**i**, **6p**−**r**, **6u**)[12] or *tert*-butyloxycarbonyl-(Boc) protected under the standard conditions (procedure B, for compounds **6j**−**o**, **6s**, **6t**, Boc$_2$O = di-*tert*-butyl dicarbonate, DMAP = 4-dimethylaminopyridine) to obtain variously substituted *N*-alkoxycarbonyl-*N*-aryl-*β*-enaminones **6a**−**u** in moderate to good yields (Scheme 2). These enaminones were subjected to irradiation at λ = 366 nm to obtain the respective *cis*-hexahydrocarbazol-4-ones. As evident from Scheme 3, the yields of *cis*-hexahydrocarbazol-4-ones were good to excellent. Enaminone **6b** with a tethered alkene exclusively went through [6π] photocyclization to give **8b** in 85% yield, and a [2 + 2] photocycloaddition product was not detected. L-Menthol as a potential chiral auxiliary did not influence the photoreaction, and **8c** was isolated in 95% yield with a diastereomeric ratio (dr) of 1:1. Protecting groups like fluorenylmethyloxycarbonyl (Fmoc), carboxybenzyl (Cbz), and Boc were well tolerated, giving the desired compounds in good to excellent yields (**8d**, **8f**, **8j**, **8m**, **8n**). Substitutions like phenyl, propargyl, bromine,

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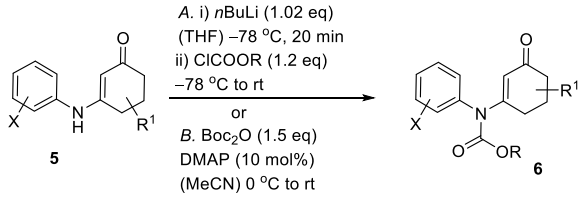
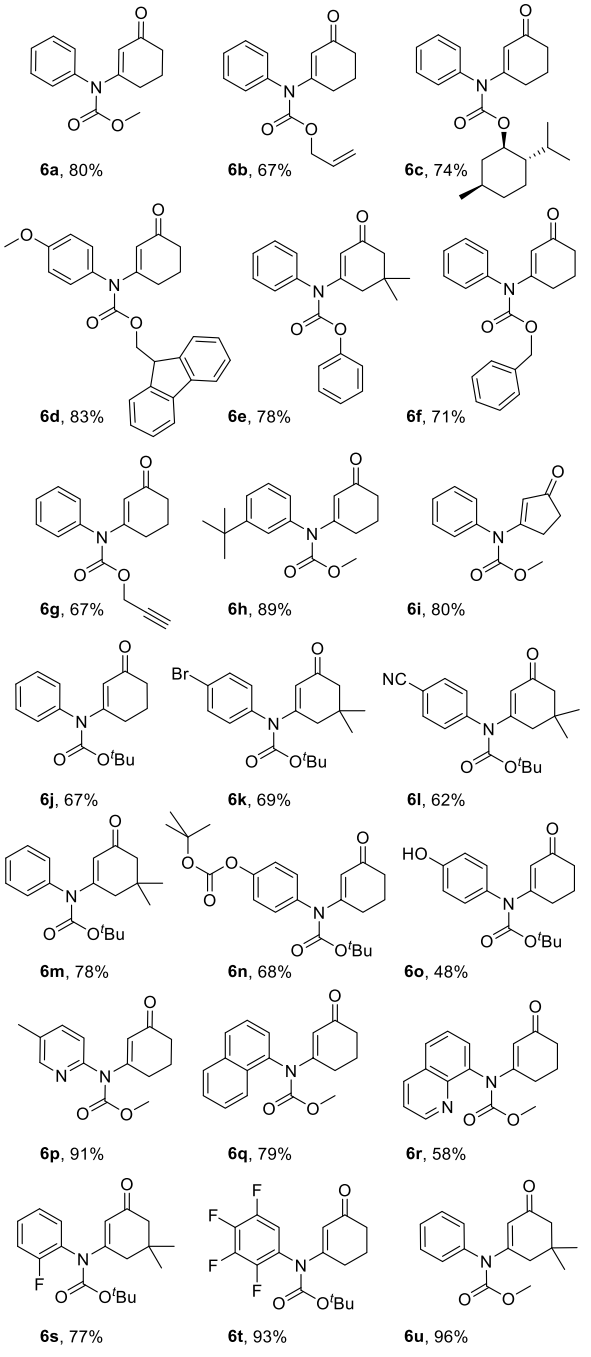
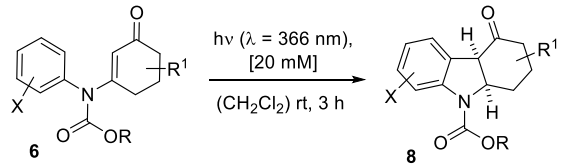
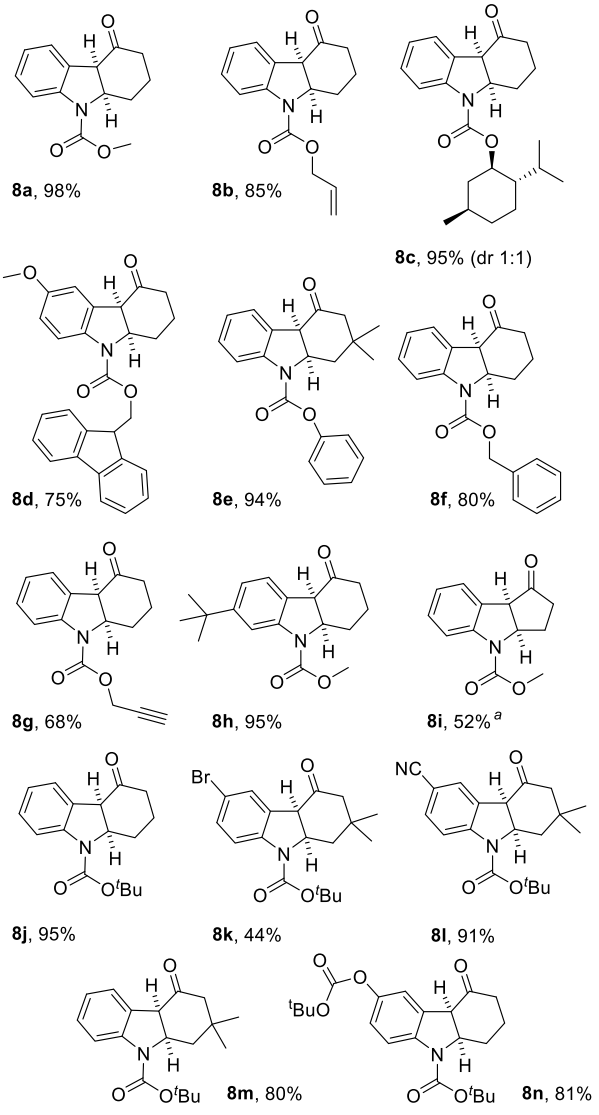
Scheme 2. Synthesis of Variously Substituted *N*-Alkoxycarbonyl-*N*-aryl-*β*-enaminones 6a−u





Scheme 3. [6π] Photocyclization to *cis*-Hexahydrocarbazol-4-ones 8a−n*





*All reactions were carried out with 0.2 mmol of **6** using degassed and dried dichloromethane (10 mL) as solvent in a Duran phototube under argon at 366 nm for 3 h. Complete epimerization was observed after silica gel column chromatography in all cases. [a]Irradiated at 300 nm for 20 h.

and nitrile were also accommodated nicely, producing *cis*-hexahydrocarbazol-4-ones in moderate to excellent yields (**8e**, **8g**, **8k**, **8l**). Interestingly, substrate **6h** with a *tert*-butyl substitution in the *meta* position on phenyl produced **8h** with complete regioselectivity in which the photocyclization took place in the position *para* to the sterically bulky *tert*-butyl group but not in the *ortho* position. Cyclopentene enaminone **6i** gave no conversion at 366 nm but rather produced the expected product at an irradiation wavelength of λ = 300 nm. A longer reaction time of 20 h was required, and *cis*-product **8i** could be isolated in a moderate yield of 52%. Enaminones **6o** and **6p** did not give any conversion and were reisolated quantitatively, suggesting that free hydroxyphenyl and 2-pyridyl as aryl components are not compatible with the [6π] photocyclization. *Ortho* substitution on phenyl was not

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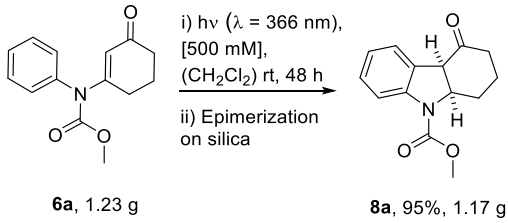
tolerated due to steric reasons, and thus, no reaction occurred upon irradiation of enaminones **6q–s**. While tetrafluoro-substituted enaminone **6t** produced a complex reaction mixture upon irradiation, substrate **6u** gave a spot-to-spot conversion but the *cis* product was found to decompose slowly at room-temperature storage.

A gram-scale reaction was carried out at a very high substrate concentration of 500 mM (Scheme 4). As expected, a longer

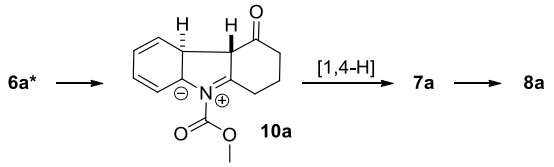
Scheme 4. Gram-Scale [6π] Photocyclization at 500 mM Concentration



irradiation time of 48 h was required for complete conversion, but to our delight, product **8a** could be isolated in an excellent yield of 95% (1.17 g). It is interesting to note that the decomposition of photoproduct that was observed with a longer irradiation time of 20 h (Table 1, entry 4) at 20 mM concentration did not occur in the scale-up reaction. This is likely because the molar absorption coefficient of starting enaminone is higher than that of the *trans*-photoproduct, and until all starting material is consumed the photoproduct does not significantly decompose.

Mechanism and DFT Calculations. On the basis of previous work,[5,6,13] the reaction course of a [6π] photocyclization is suggested to include a conrotatory ring closure as depicted for photoexcited substrate **6a*** in Scheme 5. The

Scheme 5. Mechanistic Picture of the [6π] Photocyclization



subsequent rearrangement of zwitterion **10a** to the primary product **7a** is typically formulated as a supramolecular [1,4] hydrogen shift ([1,4-H]), but there have been also suggestions that the rearrangement occurs by two consecutive suprafacial [1,2] migrations ([1,2-H]) which would lead to the same result. Subsequent epimerization of product **7a** to the *cis*-product **8a** is clearly an ionic reaction, which is promoted by acid presumably via an enol intermediate.

To shed some light on the nature of the photoexcited state **6a*** that undergoes the photocyclization, its detailed mechanism, as well as on the subsequent hydrogen shift (leading to **7a**), quantum-chemical calculations using density functional theory (DFT) as well as linear-response time-dependent DFT (TDDFT) were performed as implemented in Q-Chem 5.0.[14] In a first step, the equilibrium geometry of the substrate **6a** was optimized at the theoretical level of DFT/B3LYP/6-31G*,[15] which is by no means planar, but instead the π-systems of the bond-forming carbon atoms face each other with an interatomic distance of 3.5 Å (cf. Figures 1 and 2). To understand the light-activated photocyclization, i.e., the

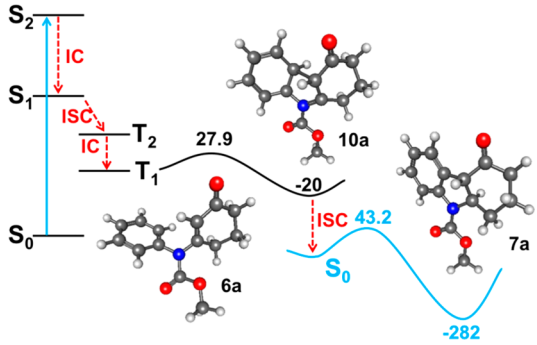


Figure 2. Computation-based reaction pathway for the photocyclization of **6a**. After excitation of **6a**, internal conversion and intersystem crossing led to the equilibrium structure of the T_1 state. In the T_1 state, photocyclization takes place (black curve) to yield **10a**. After return to the ground state, [1,4] hydrogen shift takes place (blue curve). Barrier heights and reaction energies are given in kJ/mol relative to the substrate of the reaction.

C–C bond formation, the energetically lowest excited electronic singlet and triplet states were computed at the theoretical level of TDDFT[16] using the long-range corrected CAM-B3LYP exchange-correlation functional and the 6-31G* basis set.[17] CAM-B3LYP has been found recently[18] to yield accurate results for the excitation energies of the relevant S_1, S_2, T_1, and T_2 states and also for charge-transfer excited states of organic compounds. Since the state order does not change when exchange functionals with varying amounts of nonlocal orbital exchange are used, **6a** and its photocyclization can thus be reliably described with TDDFT.

The lowest excited singlet S_1 state exhibits a computed excitation energy of 3.83 eV at TDDFT/CAM-B3LYP level and practically no oscillator strength. In the single-particle picture, this state is well represented by a HOMO–1 to LUMO transition (Figure 1), and its character is mostly of $n\pi^*$ type. However, due to the nonplanarity of **6a**, the *n*-orbital of the carbonyl oxygen mixes with the π-system of the adjacent

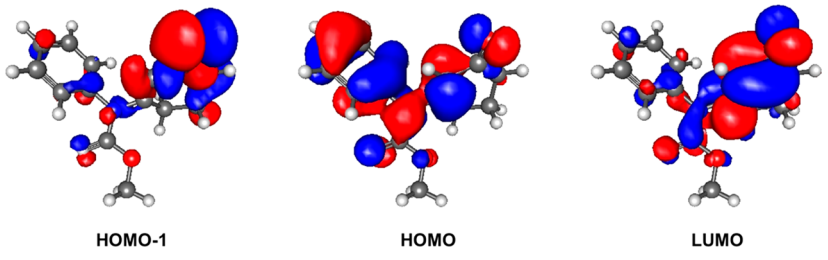


Figure 1. Frontier molecular orbitals of **6a**.

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benzene ring to the HOMO-1. The S_2 state is found at 4.91 eV with a substantial oscillator strength of 0.31. This state corresponds to the peak in the experimental absorption spectrum observed at 280 nm and is the HOMO−LUMO transition with essentially $\pi\pi^*$ excitation character (Figure 1).

For the photocyclization to proceed, the energetically low-lying triplet states are relevant, and it is expected that the presence of triplet quenchers reduces the experimental reaction yield substantially (vide infra). Since singlet−triplet intersystem crossing (ISC) is usually slower than internal conversion, ISC will occur at the relaxed equilibrium geometry of the S_1 state. At this geometry, optimized at the TDDFT/CAM-B3LYP level, the $n\pi^*$ S_1 state exhibits an excitation energy of 3.2 eV corresponding to a fluorescence wavelength of 387 nm. The overall geometrical structure of **6a** does not change; in particular, the relevant C−C distance of the bond-forming coordinate is not altered.

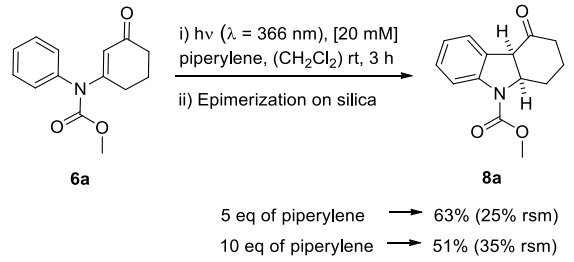
The lowest triplet state T_1 has an excitation energy of 2.66 eV and has the same electronic structure as S_1, i.e., it is the same $n\pi^*$ state. Interestingly, at 2.76 eV the T_2 state is found, which has the same electronic structure as S_2, i.e., it is represented as a HOMO−LUMO transition with $\pi\pi^*$ character (Figure 1). This energetic ordering allows for efficient ISC according to El-Sayed's rules,[19] which predicts a high ISC rate for S_1 ($n\pi^*$) → T_2 ($\pi\pi^*$). Having arrived in the triplet excitation manifold, the excited molecules decay further via internal conversion, and the photocyclization reaction proceeds in T_1.

Starting at the T_1 equilibrium structure of **6a**, we have computed the minimum energy reaction pathway for the photocyclization reaction by using unrestricted Kohn−Sham DFT in combination with the B3LYP functional with D3 dispersion correction and the 6-31G* basis set.[20] Only the distance between the C−C bond-forming atoms has been constrained, and all other geometrical parameters were allowed to relax freely along the path. Following this approach, an energy barrier of only 27.9 kJ/mol has been found for the photocyclization reaction, which considering the thermal excess excitation energy of 42.5 kJ/mol after ISC is readily accessible. For comparison, the energy barrier for photocyclization has also been computed in the singlet S_0 ground state as well as the first singlet excited state S_1, and much higher energy barriers have been found with values of 256 and 120 kJ/mol, respectively. Hence, the photocyclization clearly proceeds in the T_1 state, in particular, as in addition the intermediate photoproduct **10a** is 20 kJ/mol more stable in the triplet state than **6a** at the theoretical level of DFT/B3LYP.

After ylide **10a** is formed the molecule arrives most likely at the electronic ground state before undergoing a terminal hydrogen shift to form the *trans*-product **7a**. To answer the question whether the hydrogen shift occurs via one [1,4] or two consecutive [1,2] shifts, both pathways were computed at the theoretical level of DFT-D3/B3LYP. In both computations, only the distance between the transferred hydrogen and the acceptor carbon atom was constrained and all other parameters were freely optimized along the reaction path. According to these calculations, the hydrogen shift clearly occurs via a [1,4] mechanism, since the energy barrier exhibits only 43.2 kJ/mol, while the [1,2] shift would require 178 kJ/mol. The [1,4] hydrogen shift is in addition largely exothermic with a computed reaction energy of −282 kJ/mol. The [1,4] shift is also unlikely to occur in the triplet T_1 state since an energy barrier of at least 213 kJ/mol was computed at the DFT-D3/B3LYP level.

The calculated reaction course via a triplet intermediate T_1 was further substantiated by quenching experiments. The reactions were performed qualitatively by adding a triplet quencher to the reaction mixture and monitoring the reaction yield after a reaction time of 3 h. The reaction in the absence of a quencher had led to a complete conversion and to formation of product **8a** in 98% yield (vide supra). Addition of 5 and 10 equiv of *trans*-piperylene[21] to the reaction mixture led under standard irradiation conditions to a significant rate reduction and furnished only 63% and 51% of **8a**, respectively (Scheme 6). Unreacted starting material was recovered, indicating that

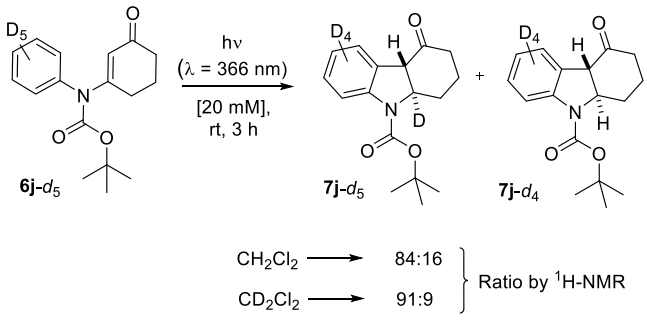
Scheme 6. Qualitative Triplet Quenching Experiments with *trans*-Piperylene



the triplet quencher reduces the reaction rate, and it was also seen that a higher quencher concentration correlates with a lower reaction rate. Further studies to completely suppress the reaction by increasing the piperylene concentration were not performed.

The fate of the migrating hydrogen atom was studied via the deuterium-labeled enaminone **6j**-d_5, which was synthesized from aniline-d_5 using the standard reaction conditions (Scheme 2).[22] After an irradiation time of 3 h, ^{1}H NMR spectra revealed the presence of **7j**-d_5 and **7j**-d_4 in a ratio of 84:16 when the reaction was carried out in dichloromethane. In deuterated dichloromethane (CD_2Cl_2) the ratio increased further to 91:9 (Scheme 7). The finding provides evidence for

Scheme 7. Experiment with Deuterium-Labeled Tertiary Enaminone 6j-d_5



a suprafacial [1,4] hydrogen migration after conrotatory ring closure. It is not completely clear, though, why the deuterium incorporation is not complete, but the result with deuterated dichloromethane seems to indicate that the zwitterion **10a** is at least partially protonated by the solvent or by an acid component in the solvent. There was no evidence for deuterium incorporation at the α-position to the carbonyl group,[23] which makes it unlikely that successive [1,2]

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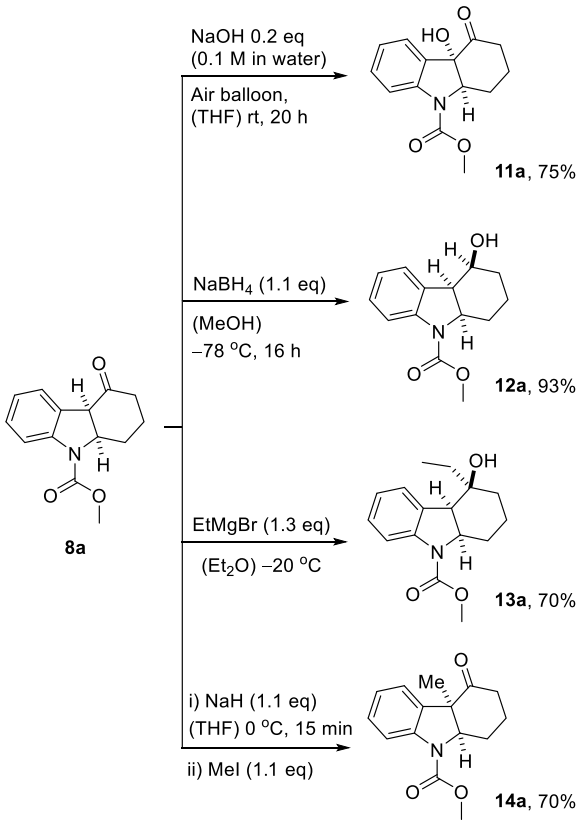
hydrogen atom migrations have occurred. This result is also in line with the calculations.

Additional Transformations. While an acid-mediated epimerization of *trans*-compound **7a** was confirmed earlier (cf. Table 1), base-mediated epimerization reactions have also been reported in the literature (Scheme 1). Following literature conditions,[7] the solvent was evaporated after irradiation of compound **6a**, and the residue was dissolved in THF under argon followed by addition of NaH (1.05 equiv) at 0 °C. After 15 min, upon quenching the enolate with water, the expected *cis*-hexahydrocarbazol-4-one **8a** could surprisingly not be detected, but a new spot was visible on TLC. Careful NMR analysis of the isolated compound and a single-crystal X-ray analysis revealed that the product was C4a-hydroxy-*cis*-hexahydrocarbazol-4-one **11a**. The compound is likely formed by diastereoselective oxygenation of the enolate upon exposure of the basic solution to air.[24] The different reactivity profile of the *N*-alkoxycarbonyl-substituted photoproducts compared to the previously reported *N*-alkyl photoproducts (Scheme 1) is evident by this transformation. Further optimization of the oxygenation revealed that catalytic sodium hydroxide (20 mol %) under air was sufficient to perform the transformation, and the desired product **11a** was isolated in 75% yield (Scheme 8).

Scheme 8. Further Diastereoselective Transformations of *cis*-Hexahydrocarbazol-4-one 8a



The perfect diastereoselectivity of the tranformation is due to the convex shape of the intermediate enolate, and it was expected that other transformations would also proceed diastereoselectively. Indeed, reduction of the carbonyl group with sodium borohydride produced alcohol **12a** as a single diastereoisomer in an excellent yield of 93%. Grignard addition also worked with complete diastereoselectivity to furnish the addition product **13a** in 70% yield. Enolate formation with sodium hydride and quenching with methyl iodide produced C4a-methylated *cis*-hexahydrocarbazol-4-one **14a** in 70% yield. All of these transformations from compound **8a** give rise to indolines with additional substituents with a potential for being used in the synthesis of libraries of biologically interesting indoline compounds.

CONCLUSION

In summary, the introduction of an acceptor substitution, namely alkoxy- and aryloxycarbonyl, at the nitrogen atom of *N*-aryl-β-enaminones allowed us to isolate stable *cis*-products from the [6π] photocyclization reaction after column purification. The labile *trans*-products could be identified as intermediates but epimerized rapidly on silica. The mechanism of the reaction could be elucidated, and further diastereoselective transformations were performed which illustrate the potential of the [6π] photocyclization products. Indeed, one direction of future research relates to total synthetic applications of the reaction. Another intriguing aspect of the *N*-alkoxycarbony-*N*-aryl-β-enaminones is their strong response to Lewis acid coordination, which might enable enantioselective transformations with chiral Lewis acids.

EXPERIMENTAL SECTION

General Methods. Air- and moisture-sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Irradiation experiments were conducted in a photochemical reactor equipped with 16 fluorescence lamps (λ_{max} = 366 nm). Dry tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and diethyl ether (Et_2O) were obtained from a solvent purification system. Other dry solvents, e.g., methanol (MeOH), were obtained in the highest purity available stored over molecular sieves. Solvents for photoreactions were degassed via a freeze–pump–thaw method and stored over molecular sieves under inert atmosphere. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 (F_{254}) glass plates. The TLC plates were visualized by either ultraviolet (UV) light (λ = 254 nm) or treatment with $KMnO_4$ stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel 60 (230–400 mesh). All solvents for chromatography, e.g., ethyl acetate (EtOAc), were distilled prior to use. NMR spectra were measured on either a 300, 400, or 500 MHz nuclear magnetic resonance spectrometer. The NMR spectra were calibrated against the residual solvent, e.g., chloroform (^{1}H NMR: δ = 7.26 ppm, ^{13}C{^{1}H} NMR: δ = 77.16 ppm). Data for ^{1}H NMR spectra were reported as follows: chemical shift in parts per million (ppm), peak shape (s = singlet, d = dublet, t = triplet, q = quartet, quin = quintet, h = sextet, m = multiplet, br = broad, virt = virtual), coupling constant in hertz (Hz), and integration. Infrared spectra were recorded by attenuated total reflection (ATR) technique and are reported as wave numbers $\tilde{\nu}$ (cm^{-1}). High-resolution mass spectrometry (HRMS) was performed by electrospray ionization (ESI) on a linear ion trap instrument with a Fourier transform ion cyclotron resonance detector. UV/vis spectra were recorded on a Lambda 35 UV/vis spectrometer using a precision cell made of quartz with a pathway of 1 mm.

General Experimental Procedure for the Synthesis of 5a–m. A mixture of the 1,3-cyclohexanedione (1.0 equiv), aniline (1.0 equiv), and $Yb(OTf)_3$ (2 mol %) in dry acetonitrile (0.5 mL/mmol) was stirred at room temperature overnight under argon. After completion of the reaction as indicated by thin-layer chromatography (100% EtOAc), the mixture was diluted by dichloromethane (5 mL/mmol). Insoluble catalyst removed by filtration followed by evaporation of volatiles under reduced pressure furnished a residue which was triturated in pentane and EtOAc (v/v = 3:1). Filtration, washing with pentane, and drying afforded **5a–m**.

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*3-(Phenylamino)cyclohex-2-en-1-one (**5a**).* According to the general procedure, compound **5a** was synthesized starting from 1,3-cyclohexanedione (3.00 g, 26.80 mmol, 1.0 equiv) and aniline (2.44 mL, 26.8 mmol, 1.0 equiv). Yellow solid (4.66 g, 93%), mp 177−179 °C. TLC: R_f = 0.30 (EtOAc) [UV]. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.83 (s, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.18−7.11 (m, 3H), 5.31 (s, 1H), 2.51−2.49 (m, 2H), 2.16 (t, J = 6.4 Hz, 2H), 1.91−1.86 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 195.7, 161.9, 139.1, 129.1, 124.3, 123.0, 98.0, 36.4, 28.5, 21.5. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3258, 3065, 1590, 1567, 1518, 752, 702. MS (ESI): m/z = 188 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{12}H_{14}NO$ [(M + H)$^+$] = 188.1075, found = 188.1069. Data of this compound were in accordance with those reported in the literature.[11]

*3-[(4-Methoxyphenyl)amino]cyclohex-2-en-1-one (**5b**).* According to the general procedure, compound **5b** was synthesized starting from 1,3-cyclohexanedione (1.82 g, 16.24 mmol, 1.0 equiv) and 4-methoxyaniline (2.00 g, 16.24 mmol, 1.0 equiv). Off-white solid (3.42 g, 97%), mp 165−167 °C. TLC: R_f = 0.24 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.67 (s, 1H), 7.10 (virt d, J = 8.9 Hz, 2H), 6.95 (virt d, J = 8.9 Hz, 2H), 5.10 (s, 1H), 3.75 (s, 3H), 2.52−2.45 (m, 2H), 2.16−2.11 (m, 2H), 1.89−1.85 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 195.2, 162.9, 156.4, 131.6, 125.3, 114.3, 97.0, 55.2, 36.4, 28.3, 21.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3212, 3030, 2943, 1568, 1504, 1237, 802, 714. MS (ESI): m/z = 218 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{13}H_{16}NO_2$ [(M + H)$^+$] = 218.1183, found = 218.1175. Data of this compound were in accordance with those reported in literature.[11]

*5,5-Dimethyl-3-(phenylamino)cyclohex-2-en-1-one (**5c**).* According to the general procedure, compound **5c** was synthesized starting from 5,5-dimethyl-1,3-cyclohexanedione (1.00 g, 7.14 mmol, 1.0 equiv) and aniline (652 μL, 7.14 mmol, 1.0 equiv). White solid (1.51 g, 98%), mp 181−183 °C. TLC: R_f = 0.60 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.78 (s, 1H), 7.40−7.34 (m, 2H), 7.19−7.10 (m, 3H), 5.32 (s, 1H), 2.38 (s, 2H), 2.05 (s, 2H), 1.02 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 195.3, 160.0, 139.1, 129.1, 124.2, 122.9, 96.7, 50.1, 42.0, 32.2, 27.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3234, 3063, 2960, 1566, 1510, 1242, 1148, 765, 704. MS (ESI): m/z = 216 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{14}H_{18}NO$ [(M + H)$^+$] = 216.1388, found = 216.1382. Data of this compound were in accordance with those reported in literature.[25]

*3-{[3-(tert-Butyl)phenyl]amino}cyclohex-2-en-1-one (**5d**).* According to the general procedure, compound **5d** was synthesized starting from 1,3-cyclohexanedione (368 mg, 3.29 mmol, 1.0 equiv) and 3-(*tert*-butyl)aniline (490 mg, 3.29 mmol, 1.0 equiv). White solid (702 mg, 86%), mp 177−179 °C. TLC: R_f = 0.46 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.84 (s, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.18−7.15 (m, 2H), 7.00 (d, J = 8.0 Hz, 1H) 5.31 (s, 1H), 2.51−2.48 (m, 2H), 2.16 (t, J = 6.1 Hz, 2H), 1.90−1.86 (m, 2H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 195.6, 162.0, 151.8, 138.7, 128.8, 121.3, 120.1, 120.0, 97.8, 36.4, 34.4, 31.0, 28.5, 21.5. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3257, 2956, 1583, 1536, 1485, 1246, 1183, 793, 703. MS (ESI): m/z = 244 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{16}H_{22}NO$ [(M + H)$^+$] = 244.1701, found = 244.1695.

*3-(Phenylamino)cyclopent-2-en-1-one (**5e**).* According to the general procedure, compound **5e** was synthesized starting from 1,3-cyclopentanedione (350 mg, 3.57 mmol, 1.0 equiv) and aniline (326 μL, 3.57 mmol, 1.0 equiv). White solid (610 mg, 98%), mp 222−224 °C. TLC: R_f = 0.22 (EtOAc) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.57 (s, 1H), 7.37−7.33 (m, 2H), 7.19 (d, J = 7.9 Hz, 2H), 7.09−7.06 (m, 1H), 5.41 (s, 1H), 2.73−2.70 (m, 2H), 2.24−2.21 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 203.9, 171.8, 140.4, 129.2, 123.4, 119.9, 100.9, 32.8, 28.4. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2990, 2950, 1738, 1704, 1598, 1481, 1443, 1276, 1055, 755. MS (ESI): m/z = 174 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{11}H_{12}NO$ [(M + H)$^+$] = 174.0919, found = 174.0913.

*3-[(4-Bromophenyl)amino]-5,5-dimethylcyclohex-2-en-1-one (**5f**).* According to the general procedure, compound **5f** was synthesized starting from 5,5-dimethyl-1,3-cyclohexanedione (800 mg, 5.70 mmol, 1.0 equiv) and 4-bromoaniline (981 mg, 5.70 mmol, 1.0 equiv). White solid (1.52 g, 89%), mp 217−219 °C. TLC: R_f = 0.63 (EtOAc) [UV]. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.84 (s, 1H), 7.52 (virt d, J = 8.6 Hz, 2H), 7.15 (virt d, J = 8.6 Hz, 2H), 5.35 (s, 1H), 2.38 (s, 2H), 2.07 (s, 2H), 1.03 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 195.6, 159.3, 138.7, 132.0, 124.5, 115.8, 97.3, 50.1, 42.0, 32.2, 27.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3239, 3172, 2957, 1568, 1401, 1147, 807, 718. MS (ESI): m/z = 335 (15) [(M + H + MeCN)$^+$], 294 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{14}H_{17}BrNO$ [(M + H)$^+$] = 294.0494, found = 294.0487. Data of this compound were in accordance with those reported in literature.[25]

*4-[(5,5-Dimethyl-3-oxocyclohex-1-en-1-yl)amino]benzonitrile (**5g**).* According to the general procedure, compound **5g** was synthesized starting from 5,5-dimethyl-1,3-cyclohexanedione (1.13 g, 8.06 mmol, 1.0 equiv) and 4-aminobenzonitrile (952 mg, 8.06 mmol, 1.0 equiv). White solid (1.90 g, 98%), mp 214−216 °C. TLC: R_f = 0.62 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.14 (s, 1H), 7.80−7.77 (m, 2H), 7.34−7.32 (m, 2H), 5.58 (s, 1H), 2.42 (s, 2H), 2.12 (s, 2H), 1.03 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 196.3, 157.8, 144.1, 133.5, 121.2, 118.9, 101.6, 100.0, 50.0, 42.1, 32.2, 27.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3260, 3185, 3101, 2957, 2226, 1606, 1573, 1510, 1243, 831, 717. MS (ESI): m/z = 341 (65) [(M + H + NH$_4$ + 2MeCN)$^+$], 282 (25) [(M + H + MeCN)$^+$], 241 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{15}H_{17}N_2O$ [(M + H)$^+$] = 241.1341, found = 241.1335. Data of this compound were in accordance with those reported in literature.[26]

*3-[(4-Hydroxyphenyl)amino]cyclohex-2-en-1-one (**5h**).* According to the general procedure, compound **5h** was synthesized starting from 1,3-cyclohexanedione (978 mg, 8.73 mmol, 1.0 equiv) and 4-hydroxyaniline (952 mg, 8.73 mmol, 1.0 equiv). Off-white solid (1.77 g, 98%), mp 208−210 °C. TLC: R_f = 0.24 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.45 (s, 1H), 8.58 (s, 1H), 6.97 (virt d, J = 8.6 Hz, 2H), 6.77 (virt d, J = 8.6 Hz, 2H), 5.04 (s, 1H), 2.47−2.43 (m, 2H), 2.14−2.10 (m, 2H), 1.90−1.82 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 195.1, 163.3, 154.8, 129.9, 125.6, 115.6, 96.8, 36.4, 28.3, 21.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3216, 3058, 2943, 2800, 1491, 1232, 1185, 819, 716. MS (ESI): m/z = 245 (10) [(M + H + MeCN)$^+$], 204 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{12}H_{14}NO_2$ [(M + H)$^+$] = 204.1025, found = 204.1019. Data of this compound were in accordance with those reported in literature.[25]

*3-[(5-Methylpyridin-2-yl)amino]cyclohex-2-en-1-one (**5i**).* To a solution of 5-methyl-2-aminopyridine (500 mg, 4.63 mmol, 1.0 equiv) in toluene (20 mL) at room temperature were added 1,3-cyclohexanedione (648 mg, 5.78 mmol, 1.25 equiv) and *p*-toluenesulfonic acid monohydrate (176 mg, 0.93 mmol, 0.2 equiv).[27] The reaction mixture was refluxed for 5 h and complete conversion was confirmed by thin-layer chromatography (methanol/EtOAc 5:95). The reaction mixture was treated with 5% aqueous $NaHCO_3$ (30 mL) and extracted with dichloromethance (40 mL × 3). Combined organic layers dried over anhydrous sodium sulfate and evaporated under reduced pressure to obtain a residue which was dry loaded on silica gel column chromatography and purified (methanol/EtOAc 1:50). Compound **5i** was isolated. Light yellow solid (625 mg, 67%), mp 159−151 °C. TLC: R_f = 0.30 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.16 (s, 1H), 813−8.12 (m, 1H), 7.53 (ddd, J = 8.4, 2.4, 0.5 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.73 (s, 1H), 2.55−2.50 (m, 2H), 2.22−2.16 (m, 5H), 1.95−1.86 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 197.2, 158.2, 152.0, 147.0, 138.4, 126.2, 113.4, 104.0, 36.4, 28.7, 21.6, 17.2. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3287, 3197, 2934, 1574, 1475, 1284, 1137, 827, 738. MS (ESI): m/z = 203 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{12}H_{15}N_2O$ [(M + H)$^+$] = 203.1184, found = 203.1178. Data of this compound were in accordance with those reported in literature.[27]

*3-(Naphthalen-1-ylamino)cyclohex-2-en-1-one (**5j**).* According to the general procedure, compound **5j** was synthesized starting from 1,3-cyclohexanedione (785 mg, 7.00 mmol, 1.0 equiv) and 1-naphthylamine (1.00 g, 7.00 mmol, 1.0 equiv). Light yellow solid (1.52 g, 92%), mp 182−184 °C. TLC: R_f = 0.35 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.02 (s, 1H), 8.01−7.87 (m, 3H), 7.59−7.53 (m, 3H), 7.40 (d, J = 7.3 Hz, 1H), 4.67 (s, 1H), 2.69−2.65 (m, 2H), 2.18−2.13 (m, 2H), 1.99−1.91 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 195.1, 164.6, 134.6, 134.0, 129.0, 128.2, 126.6,

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126.3, 126.3, 125.7, 124.0, 122.9, 98.0, 36.4, 28.0, 21.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3235, 3029, 1564, 1514, 1246, 1184, 1140, 774. MS (ESI): m/z = 238 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{16}H_{16}NO$ [$(M + H)^+$] = 238.1232, found = 238.1226. Data of this compound were in accordance with those reported in literature.[28]

*3-(Quinolin-8-ylamino)cyclohex-2-en-1-one (**5k**).* According to the procedure used for **5i**, compound **5k** was synthesized starting from 1,3-cyclohexanedione (353 mg, 3.15 mmol, 1.0 equiv) and 8-aminoquinoline (500 mg, 3.47 mmol, 1.1 equiv). Light brown solid (566 mg, 68%), mp 117−119 °C. TLC: R_f = 0.35 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.05 (s, 1H), 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.42 (dd, J = 8.3, 1.7 Hz, 1H), 7.75−7.58 (m, 4H), 5.60 (s, 1H), 2.72 (t, J = 6.1 Hz, 2H), 2.25−2.21 (m, 2H), 1.99−1.90 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 196.2, 161.1, 149.3, 140.5, 136.5, 135.4, 128.5, 126.6, 123.0, 122.2, 120.3, 100.0, 36.4, 28.9, 21.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3171, 3003, 2945, 1587, 1530, 1322, 1244, 1186, 792, 767. MS (ESI): m/z = 239 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{15}H_{15}N_2O$ [$(M + H)^+$] = 239.1184, found = 239.1178. Data of this compound were in accordance with those reported in literature.[29]

*3-[(2-Fluorophenyl)amino]-5,5-dimethylcyclohex-2-en-1-one (**5l**).* According to the general procedure, compound **5l** was synthesized starting from 5,5-dimethyl-1,3-cyclohexanedione (1.20 g, 8.57 mmol, 1.0 equiv) and 2-fluoroaniline (827 μL, 8.57 mmol, 1.0 equiv). White solid (1.89 g, 94%), mp 139−141 °C. TLC: R_f = 0.67 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.65 (s, 1H), 7.35−7.23 (m, 4H), 4.86 (s, 1H), 2.40 (s, 2H), 2.05 (s, 2H), 1.03 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 195.1, 161.2, 156.0 (d, J = 247 Hz), 127.6 (d, J = 1.5 Hz), 127.5 (d, J = 7.7 Hz), 126.2 (d, J = 12.3 Hz), 124.9 (d, J = 3.6 Hz), 116.4 (d, J = 19.7 Hz), 97.0, 50.1, 41.4, 32.4, 27.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3235, 3052, 2961, 1572, 1491, 1227, 1146, 757, 682. MS (ESI): m/z = 234 (100) [$(M + H)^+$] HRMS (ESI): calcd for $C_{14}H_{17}FNO$ [$(M + H)^+$] = 234.1294, found = 234.1288. Data of this compound were in accordance with those reported in literature.[30]

*3-[(2,3,4,5-Tetrafluorophenyl)amino]cyclohex-2-en-1-one (**5m**).* According to the general procedure, compound **5m** was synthesized starting from 1,3-cyclohexanedione (1.36 g, 12.12 mmol, 1.0 equiv) and 2,3,4,5-tetrafluoroaniline (2.00 g, 12.12 mmol, 1.0 equiv). Off-white solid (2.85 g, 91%), mp 184−186 °C. TLC: R_f = 0.50 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.84 (s, 1H), 7.44−7.34 (m, 1H), 4.97 (s, 1H), 2.53−2.49 (m, 2H) 2.20−2.15 (m, 2H), 1.94−1.86 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 195.9, 162.2, 147.8−144.3 (m), 143.7−140.2 (m), 142.6−139.4 (m), 138.8−135.8 (m), 123.4 (m), 109.5 (dd, J = 20.5, 2.1 Hz), 99.7, 36.3, 27.7, 21.4. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3205, 3059, 2962, 1573, 1518, 1488, 1187, 1135, 1063, 949, 715. MS (ESI): m/z = 301 (60) [$(M + H + MeCN)^+$], 260 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{12}H_{10}F_4NO$ [$(M + H)^+$] = 260.0699, found = 260.0692.

*3-[(Phenyl-d_5)amino]cyclohex-2-en-1-one (**5a**-d_5).* According to the general procedure, compound **5a**-d_5 was synthesized starting from 1,3-cyclohexanedione (343 mg, 3.06 mmol, 1.0 equiv) and aniline-d_5 (279 μL, 3.06 mmol, 1.0 equiv). Yellow solid (555 mg, 94%), mp 177−179 °C. TLC: R_f = 0.30 (EtOAc) [UV]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.82 (s, 1H), 5.31 (s, 1H), 2.51−2.49 (m, 2H), 2.19−2.14 (m, 2H), 1.93−1.85 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 195.7, 161.8, 138.9, 128.5 (t, J = 25.0 Hz), 122.9−122.2 (m), 97.9, 36.4, 28.5, 21.5. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3258, 3065, 1590, 1567, 1518, 752, 702. MS (ESI): m/z = 193 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{12}{}^1H_9{}^2H_5NO$ [$(M + H)^+$] = 193.1389, found = 193.1383.

General Experimental Procedure for the Synthesis of 6 (Procedure A). To a solution of **5** (1.0 equiv) in tetrahydrofuran (5 mL/mmol) was added *n*-butyllithium (2.5 M in hexane, 1.03 equiv) dropwise at −78 °C and the mixture stirred at this temperature for 20 min. Chloroformate (1.2 equiv) added dropwise followed by stirring for 1 h at −78 °C, and the temperature was allowed to rise to room temperature. After completion of the reaction as indicated by thin-layer chromatography (100% EtOAc), the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (20 mL/mmol). Washing with water (50 mL) and brine (50 mL) followed by drying on anhydrous sodium sulfate and evaporation afforded a residue. Column chromatographic purification (dry loading, pentane/EtOAc eluent system) afforded tertiary enaminones **6**.

General Experimental Procedure for the Synthesis of 6 (Procedure B). To a solution of **5** (1.0 equiv) in anhydrous acetonitrile (5 mL/mmol) were added 4-dimethylaminopyridine (10 mol %) and di-*tert*-butyl dicarbonate (1.5 equiv) at 0 °C, and the mixture was stirred at this temperature for 15 min. The temperature was allowed to rise to room temperature and the mixture stirred overnight. After completion of the reaction as indicated by thin-layer chromatography (100% EtOAc), the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (20 mL/mmol). Washing with water (50 mL) and brine (50 mL) followed by drying on sodium sulfate and evaporation of volatiles afforded a residue. Column chromatographic purification (dry loading, pentane/EtOAc eluent system) afforded tertiary enaminones **6**.

*Methyl N-(3-Oxocyclohex-1-en-1-yl)-N-phenylcarbamate (**6a**).* According to the general procedure A, compound **6a** was synthesized starting from **5a** (4.00 g, 21.36 mmol, 1.0 equiv) and methyl chloroformate (1.98 mL, 25.63 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. White solid (4.20 g, 80%), mp 100−102 °C. TLC: R_f = 0.53 (pentane/EtOAc 1:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44−7.32 (m, 3H), 7.14−7.10 (m, 2H), 5.45 (s, 1H), 3.70 (s, 3H), 2.85−2.80 (m, 2H), 2.38−2.34 (m, 2H), 2.07−1.98 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 199.2, 162.2, 153.9, 139.8, 129.6, 128.2, 128.0, 117.4, 53.6, 36.7, 29.3, 22.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 1717, 1656, 1590, 1439, 1292, 1237, 760, 706. MS (ESI): m/z = 246 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{14}H_{16}NO_3$ [$(M + H)^+$] = 246.1130, found = 246.1124.

*Allyl N-(3-Oxocyclohex-1-en-1-yl)-N-phenylcarbamate (**6b**).* According to the general procedure A, compound **6b** was synthesized starting from **5a** (1.00 g, 5.34 mmol, 1.0 equiv) and allyl chloroformate (681 μL, 6.41 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. Oil (978 mg, 67%). TLC: R_f = 0.24 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44−7.32 (m, 3H), 7.15−7.11 (m, 2H), 5.80 (ddt, J = 17.1, 10.6, 5.3 Hz, 1H), 5.46 (s, 1H), 5.16−5.05 (m, 2H), 4.59 (dt, J = 5.3, 1.5 Hz, 2H), 2.86−2.81 (m, 2H), 2.39−2.34 (m, 2H), 2.07−1.98 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 199.3, 162.4, 153.2, 139.9, 131.6, 129.7, 128.4, 128.2, 118.1, 117.5, 67.1, 36.8, 29.4, 22.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2949, 1722, 1654, 1586, 1233, 1192, 760, 705. MS (ESI): m/z = 272 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{16}H_{18}NO_3$ [$(M + H)^+$] = 272.1287, found = 272.1280.

*(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl N-(3-oxocyclohex-1-en-1-yl)-N-phenylcarbamate (**6c**).* According to the general procedure A, compound **6c** was synthesized starting from **5a** (0.50 g, 2.67 mmol, 1.0 equiv) and (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl carbonochloridate (687 μL, 3.20 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. White solid (730 mg, 74%). TLC: R_f = 0.55 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42−7.30 (m, 3H), 7.11−7.06 (m, 2H), 5.39 (s, 1H), 4.56 (td, J = 10.7, 4.3 Hz, 1H), 2.88−2.84 (m, 2H), 2.38−2.34 (m, 2H), 2.09−1.98 (m, 3H), 1.65−1.55 (m, 3H), 1.51−1.38 (m, 1H), 1.16−1.06 (m, 1H), 1.04−0.93 (m, 1H), 0.91−0.84 (m, 4H), 0.82−0.71 (m, 7H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 199.4, 162.8, 153.2, 140.0, 129.6, 128.2, 128.2, 116.5, 46.9, 40.8, 36.8, 34.1, 31.4, 29.5, 26.3, 23.4, 23.0, 22.0, 20.7, 16.4. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2950, 2928, 2869, 1721, 1652, 1584, 1241, 1203, 971, 760, 704. MS (ESI): m/z = 433 (20) [$(M + Na + MeCN)^+$], 370 (40) [$(M + H)^+$], 188 (100) [$(M - C_{11}H_{19}O_2 + 2H)^+$]. HRMS (ESI): calcd for $C_{23}H_{32}NO_3$ [$(M + H)^+$] = 370.2382, found = 370.2376.

*(9H-Fluoren-9-yl)methyl N-(4-Methoxyphenyl)-N-(3-oxocyclohex-1-en-1-yl)carbamate (**6d**).* According to the general procedure A, compound **6d** was synthesized starting from **5b** (0.50 g, 2.3 mmol,

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1.0 equiv) and (9*H*-fluoren-9-yl)methyl carbonochloridate (714 mg, 2.76 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. White solid (836 mg, 83%). TLC: R_f = 0.13 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (virt d, J = 7.5 Hz, 2H), 7.38−7.33 (m, 2H), 7.19 (td, J = 7.4, 1.1 Hz, 2H), 7.14−7.11 (m, 2H), 6.99−6.88 (m, 4H), 5.42 (s, 1H), 4.43 (d, J = 6.7 Hz, 2H), 4.03 (t, J = 6.6 Hz, 1H), 3.87 (s, 3H), 2.79−2.75 (m, 2H), 2.35−2.31 (m, 2H), 2.01−1.93 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.4, 162.7, 159.4, 153.5, 143.3, 141.3, 132.3, 129.3, 127.8, 127.0, 124.9, 120.0, 116.4, 115.0, 68.2, 55.7, 46.8, 36.7, 29.2, 22.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2950, 1723, 1648, 1586, 1508, 1236, 1192, 738. MS (ESI): m/z = 901 (10) [(2M + Na)$^+$], 503 (10) [(M + Na + MeCN)$^+$], 440 (15) [(M + H)$^+$], 218 (100) [(M − $C_{15}H_{11}O_2$ + 2H)$^+$]. HRMS (ESI): calcd for $C_{28}H_{26}NO_4$ [(M + H)$^+$] = 440.1862, found = 440.1854.

*Phenyl N-(5,5-Dimethyl-3-oxocyclohex-1-en-1-yl)-N-phenylcarbamate (**6e**).* According to the general procedure A, compound **6e** was synthesized starting from **5c** (0.50 g, 2.32 mmol, 1.0 equiv) and phenyl chloroformate (350 μL, 2.79 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 3:1, UV) afforded the product. White solid (606 mg, 78%), mp 90−92 °C. TLC: R_f = 0.46 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.41 (m, 2H), 7.40−7.30 (m, 3H), 7.26−7.17 (m, 3H), 7.07−7.03 (m, 2H), 5.51 (s, 1H), 2.79 (s, 2H), 2.24 (s, 2H), 1.10 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.3, 160.4, 152.0, 150.6, 140.0, 129.9, 129.5, 128.6, 128.0, 126.1, 121.3, 118.2, 50.6, 43.2, 34.0, 28.2. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2960, 1735, 1651, 1593, 1434, 1266, 1197, 744, 704. MS (ESI): m/z = 336 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{21}H_{22}NO_3$ [(M + H)$^+$] = 336.1600, found = 336.1594.

*Benzyl N-(3-Oxocyclohex-1-en-1-yl)-N-phenylcarbamate (**6f**).* According to the general procedure A, compound **6f** was synthesized starting from **5a** (0.30 g, 1.60 mmol, 1.0 equiv) and benzyl chloroformate (275 μL, 1.92 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. Off-white solid (365 mg, 71%), mp 64−66 °C. TLC: R_f = 0.24 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.35 (m, 3H), 7.33−7.28 (m, 3H), 7.17−7.10 (m, 4H), 5.45 (s, 1H), 5.14 (s, 2H), 2.85−2.82 (m, 2H), 2.37−2.34 (m, 2H), 2.05−1.98 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.4, 162.4, 153.3, 139.9, 135.5, 129.7, 128.6, 128.4, 128.3, 128.2, 127.7, 117.4, 68.2, 36.8, 29.4, 22.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3062, 3035, 2953, 1717, 1657, 1589, 1235, 1203, 759, 690. MS (ESI): m/z = 385 (50) [(M + Na + MeCN)$^+$], 322 (35) [(M + H)$^+$], 188 (100) [(M − $C_8H_7O_2$ + 2H)$^+$]. HRMS (ESI): calcd for $C_{20}H_{20}NO_3$ [(M + H)$^+$] = 322.1443, found = 322.1437.

*Prop-2-yn-1-yl N-(3-Oxocyclohex-1-en-1-yl)-N-phenylcarbamate (**6g**).* According to the general procedure A, compound **6g** was synthesized starting from **5a** (0.50 g, 2.67 mmol, 1.0 equiv) and prop-2-yn-1-yl carbonochloridate (313 μL, 3.20 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. Light brown solid (482 mg, 67%), mp 83−85 °C. TLC: R_f = 0.24 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45−7.33 (m, 3H), 7.16−7.13 (m, 2H), 5.48 (s, 1H), 4.68 (d, J = 2.4 Hz, 2H), 2.85−2.81 (m, 2H), 2.46 (t, J = 2.4 Hz, 1H), 2.39−2.35 (m, 2H), 2.08−1.99 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.3, 162.1, 152.7, 139.6, 128.8, 128.5, 128.1, 118.3, 75.4, 54.0, 36.8, 29.4, 22.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3174, 2945, 2118, 1729, 1642, 1589, 1235, 1192, 714, 694. MS (ESI): m/z = 270 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{16}H_{16}NO_3$ [(M + H)$^+$] = 270.1130, found = 270.1124.

*Methyl N-(3-tert-Butylphenyl)-N-(3-oxocyclohex-1-en-1-yl)-carbamate (**6h**).* According to the general procedure A, compound **6h** was synthesized starting from **5d** (0.30 g, 1.23 mmol, 1.0 equiv) and methyl chloroformate (114 μL, 1.48 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. Oil (330 mg, 89%). TLC: R_f = 0.37 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.36 (m, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 1.9 Hz, 1H), 6.92 (ddd, J = 7.5, 1.9, 1.9 Hz, 1H), 5.45 (s, 1H), 3.70 (s, 3H), 2.84−2.81 (m, 2H), 2.38−2.35 (m, 2H), 2.06−1.99 (m, 2H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 199.5, 162.6, 154.2, 153.3, 139.3, 139.7, 129.3, 125.4, 125.1, 125.1, 117.3, 53.7, 36.8, 34.9, 31.3, 29.4, 23.0. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 1727, 1651, 1594, 1437, 1294, 1235, 1199, 1068, 768, 699. MS (ESI): m/z = 365 (8) [(M + Na + MeCN)$^+$], 302 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{18}H_{24}NO_3$ [(M + H)$^+$] = 302.1756, found = 302.1750.

*Methyl N-(3-Oxocyclopent-1-en-1-yl)-N-phenylcarbamate (**6i**).* According to the general procedure A, compound **6i** was synthesized starting from **5e** (0.50 g, 2.89 mmol, 1.0 equiv) and methyl chloroformate (268 μL, 3.47 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:2, UV) afforded the product. Oil (534 mg, 80%). TLC: R_f = 0.70 (EtOAc) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49−7.41 (m, 3H), 7.20−7.15 (m, 2H), 5.49 (t, J = 1.4 Hz, 1H), 3.73 (s, 3H), 2.98−2.95 (m, 2H), 2.43−2.40 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 206.4, 173.6, 153.6, 139.6, 129.8, 129.0, 128.0, 115.3, 54.0, 34.4, 30.3. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 1736, 1673, 1569, 1436, 1281, 1241, 1171, 1057, 765, 693. MS (ESI): m/z = 273 (10) [(M + H + MeCN)$^+$], 232 (35) [(M + H)$^+$], 174 (100) [(M − $C_2H_3O_2$ + 2H)$^+$]. HRMS (ESI): calcd for $C_{13}H_{14}NO_3$ [(M + H)$^+$] = 232.0974, found = 232.0968.

*tert-Butyl N-(3-Oxocyclohex-1-en-1-yl)-N-phenylcarbamate (**6j**).* According to the general procedure B, compound **6j** was synthesized starting from **5a** (0.50 g, 2.67 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. White solid (514 mg, 67%), mp 131−133 °C. TLC: R_f = 0.30 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39−7.36 (m, 2H), 7.32−7.28 (m, 1H), 7.10−7.08 (m, 2H), 5.41 (s, 1H), 2.82−2.80 (m, 2H), 2.37−2.34 (m, 2H), 2.04−1.99 (m, 2H), 1.38 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.4, 162.8, 152.5, 140.7, 129.5, 128.1, 127.9, 117.0, 82.7, 36.8, 29.7, 28.0, 23.0. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2972, 1719, 1642, 1582, 1297, 1243, 1151, 758, 702. MS (ESI): m/z = 575 (40) [(2M + H)$^+$], 351 (35) [(M + Na + MeCN)$^+$], 288 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{17}H_{22}NO_3$ [(M + H)$^+$] = 288.1600, found = 288.1593.

*tert-Butyl N-(4-Bromophenyl)-N-(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)carbamate (**6k**).* According to the general procedure B, compound **6k** was synthesized starting from **5f** (0.50 g, 1.70 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. White solid (466 mg, 69%), mp 115−117 °C. TLC: R_f = 0.66 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (virt d, J = 8.7 Hz, 2H), 6.97 (virt d, J = 8.7 Hz, 2H), 5.38 (s, 1H), 2.66 (s, 2H), 2.22 (s, 2H), 1.41 (s, 9H), 1.09 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.2, 160.4, 152.1, 140.0, 132.8, 129.7, 121.6, 117.2, 83.2, 50.5, 43.5, 34.0, 28.2, 28.1. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2960, 1717, 1653, 1608, 1476, 1239, 1145, 834, 759. MS (ESI): m/z = 789 (30) [(2M + H)$^+$], 394 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{19}H_{25}BrNO_3$ [(M + H)$^+$] = 394.1018, found = 394.1012.

*tert-Butyl N-(4-Cyanophenyl)-N-(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)carbamate (**6l**).* According to the general procedure B, compound **6l** was synthesized starting from **5g** (0.50 g, 2.08 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. Light yellow solid (440 mg, 62%), mp 94−96 °C. TLC: R_f = 0.46 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (virt d, J = 8.7 Hz, 2H), 7.24 (virt d, J = 8.7 Hz, 2H), 5.41 (s, 1H), 2.62 (s, 2H), 2.24 (s, 2H), 1.42 (s, 9H), 1.10 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 198.9, 159.6, 151.6, 145.0, 133.4, 128.5, 119.3, 118.1, 111.4, 83.8, 50.6, 43.5, 34.0, 28.2, 28.1. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2980, 2227, 1711, 1651, 1592, 1272, 1241, 1147, 834, 766. MS (ESI): m/z = 681 (25) [(2M + H)$^+$], 341 (20) [(M + H)$^+$], 241 (100) [(M − $C_5H_9O_2$ + 2H)$^+$]. HRMS (ESI): calcd for $C_{20}H_{25}N_2O_3$ [(M + H)$^+$] = 341.1865, found = 341.1859.

*tert-Butyl N-(5,5-Dimethyl-3-oxocyclohex-1-en-1-yl)-N-phenylcarbamate (**6m**).* According to the general procedure B, compound **6m** was synthesized starting from **5c** (0.50 g, 2.32 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. White solid (571 mg, 78%), mp 111−113 °C. TLC: R_f = 0.50 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz,

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$CDCl_3$): δ 7.40−7.27 (m, 3H), 7.09−7.06 (m, 2H), 5.39 (s, 1H), 2.69 (s, 2H), 2.21 (s, 2H), 1.39 (s, 9H), 1.09 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 199.3, 160.9, 152.5, 140.9, 129.5, 128.0, 127.8, 116.7, 82.7, 50.6, 43.6, 34.0, 28.2, 28.1. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957, 1718, 1647, 1590, 1241, 1145, 758, 702. MS (ESI): *m*/*z* = 631 (50) [$(2M + H)^+$], 379 (10) [$(M + Na + MeCN)^+$], 316 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{19}H_{26}NO_3$ [$(M + H)^+$] = 316.1913, found = 316.1907.

*tert-Butyl N-{4-[(tert-Butoxycarbonyl)oxy]phenyl}-N-(3-oxocyclohex-1-en-1-yl)carbamate (**6n**).* According to the general procedure B, compound **6n** was synthesized starting from **5h** (0.50 g, 2.46 mmol, 1.0 equiv) and Boc_2O (1.34 g, 6.15 mmol, 2.5 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. White solid (675 mg, 68%), mp 153−155 °C. TLC: R_f = 0.30 (pentane/EtOAc 2:1) [UV]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (virt d, *J* = 8.9 Hz, 2H), 7.10 (virt d, *J* = 8.9 Hz, 2H), 5.50 (s, 1H), 2.76−2.73 (m, 2H), 2.37−2.33 (m, 2H), 2.04−1.97 (m, 2H), 1.56 (s, 9H), 1.38 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 199.3, 162.4, 152.3, 151.4, 150.4, 137.9, 129.0, 122.2, 117.4, 84.0, 83.0, 36.8, 29.7, 28.0, 27.8, 22.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2976, 1762, 1725, 1657, 1592, 1509, 1251, 1144, 767. MS (ESI): *m*/*z* = 829 (80) [$(2M + Na)^+$], 467 (80) [$(M + Na + MeCN)^+$], 426 (70) [$(M + Na)^+$], 404 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{22}H_{30}NO_6$ [$(M + H)^+$] = 404.2073, found = 404.2067.

*tert-Butyl N-(4-Hydroxyphenyl)-N-(3-oxocyclohex-1-en-1-yl)carbamate (**6o**).* According to the general procedure B, compound **6o** was synthesized starting from **5h** (0.50 g, 2.46 mmol, 1.0 equiv) and Boc_2O (805 mg, 3.69 mmol, 1.5 equiv). Column chromatographic purification (SiO_2, EtOAc/MeOH 98:2, UV) afforded the product as a light yellow solid (360 mg, 68%), while **6n** was also isolated in 22% yield, mp 155−157 °C. TLC: R_f = 0.30 (EtOAc) [UV]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (s, 4H), 6.46 (br, 1H), 5.49 (s, 1H), 2.48 (t, *J* = 6.2 Hz, 2H), 2.36−2.32 (m, 2H), 2.05−1.98 (m, 2H), 1.55 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 198.3, 162.2, 151.8, 148.5, 135.6, 125.2, 122.3, 100.1, 83.9, 36.8, 29.7, 27.8, 21.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3201, 2979, 2943, 1752, 1503, 1136, 828, 780. MS (ESI): *m*/*z* = 629 (15) [$(2M + Na)^+$], 304 (40) [$(M + H)^+$], 204 (100) [$(M - C_5H_9O_2 + 2H)^+$]. HRMS (ESI): calcd for $C_{17}H_{22}NO_4$ [$(M + H)^+$] = 304.1549, found = 304.1542.

*Methyl N-(5-Methylpyridin-2-yl)-N-(3-oxocyclohex-1-en-1-yl)carbamate (**6p**).* According to the general procedure A, compound **6p** was synthesized starting from **5i** (0.50 g, 2.47 mmol, 1.0 equiv) and methyl chloroformate (286 μL, 3.70 mmol, 1.5 equiv). Column chromatographic purification (SiO_2, EtOAc, UV) afforded the product. Oil (586 mg, 91%). TLC: R_f = 0.16 (Pentane/EtOAc 2:1) [UV]. ^1H NMR (400 MHz, $CDCl_3$): δ 8.34−8.33 (m, 1H), 7.58 (ddd, *J* = 8.1, 2.4, 0.7 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 5.41 (s, 1H), 3.72 (s, 3H), 2.80−2.76 (m, 2H), 2.38−2.35 (m, 5H), 2.07−2.01 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 199.4, 161.4, 153.6, 150.5, 150.0, 139.3, 133.3, 122.2, 118.0, 53.8, 36.8, 29.1, 22.6, 18.1. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2953, 1729, 1654, 1589, 1478, 1233, 1204, 759. MS (ESI): *m*/*z* = 543 (8) [$(2M + Na)^+$], 324 (10) [$(M + Na + MeCN)^+$], 261 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{14}H_{17}N_2O_3$ [$(M + H)^+$] = 261.1239, found = 261.1232.

*Methyl N-(Naphthalen-1-yl)-N-(3-oxocyclohex-1-en-1-yl)carbamate (**6q**).* According to the general procedure A, compound **6q** was synthesized starting from **5j** (0.50 g, 2.10 mmol, 1.0 equiv) and methyl chloroformate (195 μL, 2.52 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. Off-white solid (494 mg, 79%), mp 130−132 °C. TLC: R_f = 0.25 (pentane/EtOAc 4:1) [UV]. ^1H NMR (300 MHz, $CDCl_3$): δ 7.93−7.87 (m, 2H), 7.68−7.63 (m, 1H), 7.55−7.47 (m, 3H), 7.31 (dd, *J* = 7.2, 1.1 Hz, 1H), 5.40 (s, 1H), 3.62 (s, 3H), 3.06−2.85 (m, 2H), 2.37−2.33 (m, 2H), 2.08−1.99 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 199.4, 162.3, 154.4, 136.1, 134.7, 130.3, 129.3, 128.8, 127.6, 126.7, 126.5, 125.7, 121.8, 116.1, 53.9, 36.8, 29.1, 23.0. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2949, 1728, 1649, 1591, 1293, 1235, 1027, 784. MS (ESI): *m*/*z* = 337 (5) [$(M + H + MeCN)^+$], 296 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{18}H_{18}NO_3$ [$(M + H)^+$] = 296.1287, found = 296.1280.

*Methyl N-(3-Oxocyclohex-1-en-1-yl)-N-(quinolin-8-yl)carbamate (**6r**).* According to the general procedure A, compound **6r** was synthesized starting from **5k** (0.50 g, 2.10 mmol, 1.0 equiv) and methyl chloroformate (195 μL, 2.52 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:4, UV) afforded the product. Light brown solid (365 mg, 58%), mp 97−99 °C. TLC: R_f = 0.16 (pentane/EtOAc 2:1) [UV]. ^1H NMR (300 MHz, $CDCl_3$): δ 8.89 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.88−7.83 (m, 1H), 7.57−7.55 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.15 (s, 1H), 3.61 (s, 3H), 3.08 (br, 2H), 2.37−2.33 (m, 2H), 2.12−2.04 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 199.7, 164.1, 154.6, 151.2, 144.2, 137.9, 136.3, 129.5, 129.2, 128.9, 126.5, 122.0, 116.4, 53.7, 36.9, 29.4, 23.2. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2958, 1727, 1640, 1582, 1432, 1237, 1201, 1185, 1029, 791, 759. MS (ESI): *m*/*z* = 360 (15) [$(M + Na + MeCN)^+$], 297 (70) [$(M + H)^+$], 265 (100) [$(M - OMe)^+$]. HRMS (ESI): calcd for $C_{17}H_{17}N_2O_3$ [$(M + H)^+$] = 297.1239, found = 297.1232.

*tert-Butyl N-(5,5-Dimethyl-3-oxocyclohex-1-en-1-yl)-N-(2-fluorophenyl)carbamate (**6s**).* According to the general procedure B, compound **6s** was synthesized starting from **5l** (0.50 g, 2.14 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. White solid (550 mg, 77%), mp 92−94 °C. TLC: R_f = 0.67 (pentane/EtOAc 4:1) [UV]. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35−7.29 (m, 1H), 7.18−7.09 (m, 3H), 5.35 (s, 1H), 2.76 (br, 2H), 2.22 (s, 2H), 1.39 (s, 9H), 1.10 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 199.4, 160.6, 157.9 (d, *J* = 250.5 Hz), 151.8, 130.0, 129.9, 128.7 (d, *J* = 13.2 Hz), 124.9 (d, *J* = 4.0 Hz), 116.7 (d, *J* = 19.9 Hz), 115.8, 83.1, 50.6, 43.6, 34.0, 28.2, 28.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −121.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2959, 1721, 1650, 1597, 1238, 1141, 754. MS (ESI): *m*/*z* = 667 (40) [$(2M + H)^+$], 397 (10) [$(M + Na + MeCN)^+$], 334 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{19}H_{25}FNO_3$ [$(M + H)^+$] = 334.1818, found = 334.1812.

*tert-Butyl N-(3-Oxocyclohex-1-en-1-yl)-N-(2,3,4,5-tetrafluorophenyl)carbamate (**6t**).* According to the general procedure B, compound **6t** was synthesized starting from **5m** (0.50 g, 1.93 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. White solid (645 mg, 93%), mp 79−81 °C. TLC: R_f = 0.63 (pentane/EtOAc 4:1) [UV]. ^1H NMR (400 MHz, $CDCl_3$): δ 6.90−6.83 (m, 1H), 5.36 (s, 1H), 2.85−2.81 (m, 2H), 2.40−2.36 (m, 2H), 2.08−2.02 (m, 2H), 1.43 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 198.9, 161.4, 150.9, 148.3−145.6 (m), 145.5−142.9 (m), 142.9−140.1 (m), 142.0−139.2 (m), 124.8−124.6 (m), 117.5, 111.9 (dd, *J* = 20.1, 3.4 Hz), 84.3, 36.8, 29.3, 27.9, 22.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −138.1 (qd, *J* = 10.7, 1.8 Hz, 1F), −144.4 (qd, *J* = 10.7, 3.8 Hz, 1F), −153.6 (td, *J* = 20.2, 1.8 Hz, 1F), −154.1 (m, 1F). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3018, 1730, 1650, 1609, 1521, 1289, 1148, 1126, 752. MS (ESI): *m*/*z* = 719 (5) [$(2M + H)^+$], 360 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{17}H_{18}F_4NO_3$ [$(M + H)^+$] = 360.1223, found = 360.1217.

*Methyl N-(5,5-Dimethyl-3-oxocyclohex-1-en-1-yl)-N-phenylcarbamate (**6u**).* According to the general procedure A, compound **6u** was synthesized starting from **5c** (0.50 g, 2.32 mmol, 1.0 equiv) and methyl chloroformate (215 μL, 2.79 mmol, 1.2 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. Light yellow solid (608 mg, 96%), mp 77−79 °C. TLC: R_f = 0.40 (pentane/EtOAc 4:1) [UV]. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34−7.21 (m, 3H), 7.02−6.99 (m, 2H), 5.33 (s, 1H), 3.60 (s, 3H), 2.60 (s, 2H), 2.12 (s, 2H), 0.98 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 199.3, 160.5, 154.1, 140.2, 129.8, 128.3, 128.1, 117.3, 53.7, 50.5, 43.3, 34.0, 28.2. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2954, 1718, 1651, 1583, 1434, 1265, 1242, 1060, 709. MS (ESI): *m*/*z* = 274 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{16}H_{20}NO_3$ [$(M + H)^+$] = 274.1443, found = 274.1437.

*tert-Butyl N-(3-Oxocyclohex-1-en-1-yl)-N-(phenyl-d_5)carbamate (**6j**-d_5).* According to the general procedure B, compound **6j**-d_5 was synthesized starting from **5a**-d_5 (300 mg, 1.56 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. White solid (245 mg, 54%), mp 131−133

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°C. TLC: R_f = 0.30 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (s, 1H), 2.82−2.79 (m, 2H), 2.37−2.34 (m, 2H), 2.05−1.99 (m, 2H), 1.38 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 199.4, 162.9, 152.5, 140.6, 129.0 (t, J = 24.4 Hz), 127.9−127.0 (m), 117.0, 82.7, 36.8, 29.7, 28.0, 23.0. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2972, 1719, 1642, 1582, 1297, 1243, 1151, 758, 702. MS (ESI): m/z = 293 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{17}{}^1H_{17}{}^2H_5NO_3$ [$(M + H)^+$] = 293.1914, found = 293.1909.

General Experimental Procedure for the Photochemical Reaction. The substrate (0.20 mmol, 1.0 equiv) was placed in an oven-dried Duran phototube (diameter: 1 cm, volume: 12 mL). Three cycles of vacuum/argon were applied, and 10 mL of DCM (dry and degassed) was added. The mixture was irradiated at λ = 366 nm at room temperature until full conversion as confirmed by thin-layer chromatography. All volatiles were removed under reduced pressure, and the crude *trans*-photoproduct was wet loaded (1 mL DCM) for silica gel column chromatography to isolate *cis*-hexahydrocarbazol-4-ones **8**.

*Methyl 4-Oxo-1,2,3,4,4a,9a-trans-hexahydro-9H-carbazole-9-carboxylate (**7a**).* According to the general irradiation conditions, after complete conversion solvent was evaporated under reduced pressure, the residue was dissolved in methanol-d_4, and ^{1}H NMR was measured for the crude sample. The coupling constants were clear with methanol-d_4, but the compound decomposed over the time; thus, we only report ^{1}H NMR in this solvent. ^{1}H NMR (500 MHz, methanol-d_4): δ 7.71 (d, J = 8.1 Hz, 1H), 7.51−7.50 (m, 1H), 7.22−7.18 (m, 1H), 7.02 (td, J = 7.5, 0.9 Hz, 1H), 3.96 (d, J = 14.3 Hz, 1H), 3.85 (s, 3H), 3.78 (ddd, J = 14.3, 11.1, 3.3 Hz, 1H), 3.09−3.04 (m, 1H), 2.61−2.53 (m, 1H), 2.40 (ddd, J = 14.9, 5.4, 3.0 Hz, 1H), 2.26−2.20 (m, 1H), 2.11−2.03 (m, 1H), 1.87−1.78 (m, 1H). In chloroform-d_1, coupling is not clear but the compound is stable for a longer time, providing better carbon spectra. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 1H), 7.56−7.54 (m, 1H), 7.24−7.19 (m, 1H), 7.04 (td, J = 7.4. 1.0 Hz, 1H), 3.86 (s, 3H), 3.79−3.76 (m, 2H), 3.15−3.07 (m, 1H), 2.49−2.44 (m, 2H), 2.27−2.17 (m, 1H), 2.08−1.95 (m, 1H), 1.90−1.74 (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 204.9, 155.0, 143.2, 128.3, 125.7, 125.0, 123.3, 114.9, 67.0, 57.3, 52.7, 40.8, 30.6, 23.4.

*tert-Butyl 4-Oxo-1,2,3,4,4a,9a-trans-hexahydro-9H-carbazole-9-carboxylate-5,6,7,8,9a-d_5 (**7j**-d_5).* General irradiation conditions were followed, but CD_2Cl_2 was used as a reaction solvent. After complete conversion, solvent was evaporated under reduced pressure, the residue was dissolved in methanol-d_4, and ^{1}H NMR was measured for the crude sample. The ratio of **7j**-d_5 to **7j**-d_4 was found to be 91:9. ^{1}H NMR (500 MHz, methanol-d_4): δ 3.87 (s, 1H), 3.69 (ddd, J = 14.3, 11.1, 3.3 Hz, 0.09H), 3.07−3.03 (m, 1H), 2.58−2.52 (m, 1H), 2.41−2.36 (m, 1H), 2.24−2.19 (m, 1H), 2.06−2.01 (m, 1H), 1.86−1.77 (m, 1H), 1.60 (s, 9H).

*Methyl 4-Oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8a**).* According to the general procedure, compound **8a** was synthesized starting from **6a** (49 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 3:1, UV) afforded the product. White solid (48 mg, 98%), mp 102−104 °C. TLC: R_f = 0.35 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (br, 1H), 7.27−7.22 (m, 1H), 7.13−7.11 (m, 1H), 7.01−6.96 (m, 1H), 4.84−4.77 (m, 1H), 4.13 (d, J = 9.2 Hz, 1H), 3.87 (s, 3H), 2.50−2.16 (m, 3H), 1.93−1.83 (m, 1H), 1.74−1.58 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 208.1, 153.2, 141.6, 128.9, 127.5, 124.2, 123.4, 115.6, 61.3, 53.8, 52.8, 38.8, 27.7, 18.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2947, 1696, 1478, 1443, 1391, 756. MS (ESI): m/z = 506 (100) [$(2M + NH_4 - 2H)^+$], 244 (10) [$(M - H)^+$]. HRMS (ESI): calcd for $C_{14}H_{14}NO_3$ [$(M - H)^+$] = 244.0974, found = 244.0968. The structure of this compound was also confirmed by single-crystal XRD analysis (CCDC 1877642).

*Allyl 4-Oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8b**).* According to the general procedure, compound **8b** was synthesized starting from **6b** (54 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. White solid (46 mg, 85%), mp 67−69 °C. TLC: R_f = 0.54 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (br, 1H), 7.26 (m, 1H), 7.14−7.11 (m, 1H), 7.02−6.97 (m, 1H), 6.03 (ddt, J = 16.2, 10.8, 5.7 Hz, 1H), 5.42−5.36 (m, 1H), 5.31−5.27 (m, 1H), 4.88−4.76 (m, 3H), 4.14 (d, J = 9.2 Hz, 1H), 2.51−2.18 (m, 3H), 1.94−1.84 (m, 1H), 1.76−1.63 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 208.1, 152.5, 132.5, 129.0, 127.6, 124.2, 123.5, 120.7, 118.5, 115.7, 66.5, 61.4, 53.8, 38.8, 27.7, 18.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2950, 1699, 1479, 1396, 1259, 753. MS (ESI): m/z = 624 (100) [$(2M + 2MeCN)^+$], 270 (10) [$(M - H)^+$]. HRMS (ESI): calcd for $C_{16}H_{16}NO_3$ [$(M - H)^+$] = 270.1130, found = 270.1124.

*(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-Oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8c**).* According to the general procedure, compound **8c** was synthesized starting from **6c** (74 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 3:1, UV) afforded the product. White solid (70 mg, 1:1 dr, 95%). TLC: R_f = 0.60 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (br, 2H), 7.27−7.22 (m, 2H), 7.13−7.10 (m, 2H), 7.00−6.95 (m, 2H), 4.85−4.74 (m, 4H), 4.13 (d, J = 9.2 Hz, 2H), 2.50−2.27 (m, 4H), 2.19−2.12 (m, 4H), 2.04−1.84 (m, 4H), 1.76−1.63 (m, 8H), 1.56−1.46 (m, 4H), 1.19−1.02 (m, 4H), 0.98−0.91 (m, 14H), 0.84−0.81 (m, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 208.3, 208.2, 152.6, 129.0, 128.9, 127.7, 124.2, 123.2, 115.7, 115.6, 96.9, 61.2, 61.2, 53.8, 47.6, 47.5, 41.7, 41.5, 38.8, 34.4, 31.6, 26.6, 26.3, 23.7, 23.3, 22.1, 21.1, 21.0, 18.9, 16.6, 16.3. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2953, 2868, 1701, 1479, 1396, 1259, 751. MS (ESI): m/z = 368 (100) [$(M - H)^+$]. HRMS (ESI): calcd for $C_{23}H_{30}NO_3$ [$(M - H)^+$] = 368.2226, found = 368.2219.

*(9H-Fluoren-9-yl)methyl 6-Methoxy-4-oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8d**).* According to the general procedure, compound **8d** was synthesized starting from **6d** (88 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. White solid (77 mg, 87%), mp 139−141 °C. TLC: R_f = 0.30 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79−7.76 (m, 1H), 7.71−7.59 (m, 3H), 7.44−7.38 (m, 2H), 7.36−7.31 (m, 2H), 6.76−6.51 (m, 2H), 4.73 (m, 2H), 4.32−4.27 (m, 2H), 3.98 (br, 1H), 3.72 (s, 3H), 2.47−2.37 (m, 1H), 2.26−2.20 (m, 1H), 1.79−1.34 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 208.1, 156.3, 152.3, 143.9, 141.7, 141.6, 127.9, 127.9, 127.3, 124.7, 120.1, 116.2, 114.3, 109.8, 66.7, 61.4, 55.8, 53.7, 47.4, 38.8, 27.1, 18.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2948, 1700, 1488, 1267, 739. MS (ESI): m/z = 440 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{28}H_{26}NO_4$ [$(M + H)^+$] = 440.1862, found = 440.1855.

*Phenyl 2,2-Dimethyl-4-oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8e**).* According to the general procedure, compound **8e** was synthesized starting from **6e** (68 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. White solid (64 mg, 94%), mp 110−112 °C. TLC: R_f = 0.34 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92−7.66 (m, 1H), 7.46−7.41 (m, 2H), 7.33−7.22 (m, 4H), 7.17−7.15 (m, 1H), 7.09−7.03 (m, 1H), 5.12−5.05 (m, 1H), 4.19−4.16 (m, 1H), 2.38−2.27 (m, 3H), 1.66−1.48 (m, 1H), 1.05−1.03 (m, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 207.7, 150.7, 140.8, 129.6, 129.2, 127.8, 125.9, 124.0, 121.8, 116.3, 60.4, 52.8, 52.1, 40.4, 32.1, 31.1, 25.3. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957, 1703, 1475, 1385, 1203, 752. MS (ESI): m/z = 399 (300) [$(M - H + Na + MeCN)^+$], 357 (100) [$(M - H + Na)^+$]. HRMS (ESI): calcd for $C_{21}H_{20}NO_3$ [$(M - H)^+$] = 334.1443, found = 334.1438.

*Benzyl 4-Oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8f**).* According to the general procedure, compound **8f** was synthesized starting from **6f** (64 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1, UV) afforded the product. Oil (51 mg, 80%). TLC: R_f = 0.28 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (br, 1H), 7.45−7.32 (m, 5H), 7.26−7.22 (m, 1H), 7.14−7.11 (m, 1H), 7.02−6.96 (m, 1H), 5.31 (s, 2H), 4.89−4.81 (m, 1H), 4.13 (d, J = 9.2 Hz, 1H), 2.49−2.18 (m, 3H), 1.92−1.82 (m, 1H), 1.75−1.61 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 208.0, 152.5, 136.1, 129.0, 128.7, 128.4, 128.3, 127.6, 124.2, 123.5, 115.7, 67.6, 61.4, 53.8, 38.7, 27.7, 18.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2952, 1703, 1399, 1295, 1048,

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751, 696. MS (ESI): m/z = 320 (100) [$(M - H)^+$]. HRMS (ESI): calcd for $C_{20}H_{18}NO_3$ [$(M - H)^+$] = 320.1287, found = 320.1282.

*Prop-2-yn-1-yl 4-Oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8g**).* According to the general procedure compound **8g** was synthesized starting from **6g** (54 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 3:1, UV) afforded the product. White solid (37 mg, 68%), mp 97−99 °C. TLC: R_f = 0.44 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (br, 1H), 7.32−7.26 (m, 1H), 7.17−7.14 (m, 1H), 7.03 (td, J = 7.4, 1.0 Hz, 1H), 4.94−4.83 (m, 3H), 4.16 (d, J = 9.1 Hz, 1H), 2.55 (t, J = 2.4 Hz, 1H), 2.53−2.22 (m, 3H), 1.97−1.85 (m, 1H), 1.77−1.65 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 207.9, 151.7, 141.4, 129.0, 127.6, 124.2, 123.8, 115.8, 77.9, 75.3, 61.4, 53.7, 53.2, 38.7, 27.6, 18.8. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3282, 2952, 2130, 1706, 1695, 1480, 1405, 1140, 1046, 762. MS (ESI): m/z = 309 (80) [$(M - H + MeCN)^+$], 268 (100) [$(M - H)^+$]. HRMS (ESI): calcd for $C_{16}H_{14}NO_3$ [$(M - H)^+$] = 268.0974, found = 268.0969.

*Methyl 7-tert-Butyl-4-oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8h**).* According to the general procedure, compound **8h** was synthesized starting from **6h** (60 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 4:1, UV) afforded the product. Oil (57 mg, 95%). TLC: R_f = 0.60 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (500 MHz, Acetone-d_6): δ 7.91 (br, 1H), 7.05 (dd, J = 7.9, 1.8 Hz, 1H), 6.99 (dd, J = 7.9, 1.1 Hz, 1H), 4.86 (dt, J = 9.1, 5.6 Hz, 1H), 4.06 (d, J = 9.1 Hz, 1H), 3.83 (s, 3H), 2.41−2.35 (m, 1H), 2.32−2.20 (m, 2H), 1.86−1.80 (m, 1H), 1.76−1.67 (m, 1H), 1.62−1.54 (m, 1H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, Acetone-d_6): δ 206.4, 152.5, 151.6, 125.1, 123.1, 119.7, 112.2, 61.2, 53.9, 52.7, 51.8, 38.1, 34.4, 30.7, 27.2, 18.2. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 1702, 1494, 1441, 1296, 1094, 761. MS (ESI): m/z = 300 (100) [$(M - H)^+$]. HRMS (ESI): calcd for $C_{18}H_{22}NO_3$ [$(M - H)^+$] = 300.1600, found = 300.1594.

*Methyl 1-Oxo-2,3,3a,8b-cis-tetrahydrocyclopenta[b]indole-4(1H)-carboxylate (**8i**).* According to the general procedure, compound **8i** was synthesized starting from **6i** (46 mg, 0.20 mmol, 1.0 equiv) with little change. Irradiation wavelength of 300 nm and 20 h irradiation time was required. Column chromatographic purification (SiO_2, pentane/EtOAc 3:2, UV) afforded the product. White solid (24 mg, 52%), mp 138−140 °C. TLC: R_f = 0.70 (pentane/EtOAc 1:1) [UV]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (br, 1H), 7.39−7.38 (m, 1H), 7.27−7.23 (m, 1H), 7.01 (td, J = 7.5, 1.0 Hz, 1H), 5.09 (br, 1H), 3.92−3.90 (m, 4H), 2.59−2.50 (m, 1H), 2.35−2.31 (m, 2H), 2.21 (br, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 214.1, 167.4, 141.6, 129.0, 126.1, 124.9, 123.5, 115.2, 61.6, 53.2, 52.9, 35.8, 29.0. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2990, 2950, 1738, 1704, 1481, 1443, 1389, 1276, 1055, 755. MS (ESI): m/z = 273 (20) [$(M + H + MeCN)^+$], 229 (100) [$(M - 2H)^+$]. HRMS (ESI): calcd for $C_{13}H_{14}NO_3$ [$(M + H)^+$] = 232.0974, found = 232.0969.

*tert-Butyl 4-Oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8j**).* According to the general procedure, compound **8j** was synthesized starting from **6j** (58 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 3:1, UV) afforded the product. Oil (55 mg, 95%). TLC: R_f = 0.67 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (br, 1H), 7.25−7.20 (m, 1H), 7.11−7.09 (m, 1H), 6.96 (td, J = 7.5, 0.9 Hz, 1H), 4.78−4.76 (m, 1H), 4.11 (d, J = 9.0 Hz, 1H), 2.49−2.32 (m, 2H), 2.23−2.17 (m, 1H), 1.93−1.82 (m, 1H), 1.70−1.64 (m, 2H), 1.58 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 208.4, 151.8, 141.8, 128.9, 127.8, 124.2, 123.0, 115.6, 61.3, 60.5, 53.7, 38.8, 28.6, 27.7, 18.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2974, 1697, 1478, 1386, 1142, 751. MS (ESI): m/z = 327 (20) [$(M - H + MeCN)^+$], 286 (100) [$(M - H)^+$]. HRMS (ESI): calcd for $C_{17}H_{20}NO_3$ [$(M - H)^+$] = 286.1443, found = 286.1437.

*tert-Butyl 6-Bromo-2,2-dimethyl-4-oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8k**).* According to the general procedure, compound **8k** was synthesized starting from **6k** (79 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. Light yellow solid (35 mg, 44%). TLC: R_f = 0.60 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (br, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.22−7.21 (m, 1H), 4.81 (br, 1H), 4.01 (d, J = 8.9 Hz, 1H), 2.29−2.17 (m, 3H), 1.58 (s, 9H), 1.44−1.36 (m, 1H), 1.02 (s, 3H), 0.98 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 207.7, 151.4, 131.8, 129.7, 127.1, 117.3, 115.3, 60.0, 52.3, 52.0, 40.1, 31.9, 31.2, 28.5, 25.4. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957, 1705, 1473, 1137, 764. MS (ESI): m/z = 786 (100) [$(2M - 2H)^+$], 392 (50) [$(M - H)^+$]. HRMS (ESI): calcd for $C_{19}H_{23}BrNO_3$ [$(M - H)^+$] = 392.0861, found = 392.0857.

*tert-Butyl 6-Cyano-2,2-dimethyl-4-oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8l**).* According to the general procedure, compound **8l** was synthesized starting from **6l** (68 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1, UV) afforded the product. White solid (62 mg, 91%). TLC: R_f = 0.60 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (br, 1H), 7.53−7.51 (m, 1H), 7.39−7.38 (m, 1H), 4.87 (br, 1H), 4.02 (d, J = 9.1 Hz, 1H), 2.31−2.27 (m, 1H), 2.20−2.16 (m, 2H), 1.58 (s, 9H), 1.37 (t, J = 12.2 Hz, 1H), 1.03 (s, 3H), 1.00 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 206.9, 151.1, 145.2, 133.9, 128.9, 127.8, 119.0, 116.0, 105.9, 82.8, 60.1, 52.3, 51.4, 40.1, 31.7, 31.1, 28.4, 25.5. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 2223, 1715, 1482, 1382, 1145, 840, 764. MS (ESI): m/z = 281 (100) [$(M - t$Bu $- 2H)^+$], 239 (70) [$(M - Boc)^+$]. HRMS (ESI): calcd for $C_{20}H_{23}N_2O_3$ [$(M - H)^+$] = 339.1709, found = 339.1702.

*tert-Butyl 2,2-Dimethyl-4-oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8m**).* According to the general procedure, compound **8m** was synthesized starting from **6m** (64 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 4:1, UV) afforded the product. Oil (51 mg, 80%). TLC: R_f = 0.84 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85−7.45 (m, 1H), 7.25−7.20 (m, 1H), 7.09−7.06 (m, 1H), 6.95 (td, J = 7.5, 1.0 Hz, 1H), 4.83 (br, 1H), 4.03 (d, J = 8.8 Hz, 1H), 2.28−2.14 (m, 3H), 1.58 (s, 9H), 1.46−1.37 (m, 1H), 1.00 (s, 3H), 0.98 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 208.4, 151.7, 141.3, 128.9, 127.7, 124.0, 123.0, 115.9, 59.9, 52.5, 52.2, 39.9, 32.0, 31.2, 28.5, 25.3. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 1697, 1478, 1388, 1162, 750. MS (ESI): m/z = 628 (10) [$(2M - 2H)^+$], 416 (100) [$(M + 2MeCN + NH_4 + H)^+$], 314 (30) [$(M - H)^+$], 214 (15) [$(M - Boc)^+$]. HRMS (ESI): calcd for $C_{19}H_{24}NO_3$ [$(M - H)^+$] = 314.1756, found = 314.1750.

*tert-Butyl 6-[(tert-Butoxycarbonyl)oxy]-4-oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**8n**).* According to the general procedure, compound **8n** was synthesized starting from **6n** (80 mg, 0.20 mmol, 1.0 equiv). Column chromatographic purification (SiO_2, pentane/EtOAc 2:1) [UV] afforded the product. White solid (65 mg, 81%). TLC: R_f = 0.50 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (br, 1H), 7.01−6.97 (m, 1H), 6.94−6.92 (m, 1H), 4.78−4.75 (m, 1H), 4.09 (d, J = 9.4 Hz, 1H), 2.49−2.16 (m, 3H), 1.94−1.83 (m, 1H), 1.68−1.62 (m, 2H), 1.56 (s, 9H), 1.52 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 207.8, 151.1, 151.6, 146.7, 139.5, 128.7, 121.5, 117.6, 115.7, 83.5, 81.6, 61.5, 53.2, 38.8, 28.5, 27.8, 27.5, 18.7. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2977, 1754, 1698, 1483, 1389, 1240, 1132, 748. MS (ESI): m/z = 824 (40) [$(2M + NH_4)^+$], 467 (20) [$(M + Na + MeCN)^+$], 421 (100) [$(M + NH_4)^+$]. HRMS (ESI): calcd for $C_{22}H_{28}NO_6$ [$(M - H)^+$] = 402.1917, found = 402.1911.

*Methyl 4-Oxo-1,2,3,4-tetrahydro-9H-carbazole-9-carboxylate (**9a**).* This is the byproduct formed upon longer irradiation (Table 1, entry 4). Column chromatographic purification (SiO_2, pentane/EtOAc 1:1) [UV] afforded the byproduct. White solid (6 mg, 12%). TLC: R_f = 0.50 (pentane/EtOAc 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30−8.27 (m, 1H), 8.09−8.06 (m, 1H), 7.37−7.31 (m, 2H), 4.10 (s, 3H), 3.32 (t, J = 6.2 Hz, 2H), 2.62−2.57 (m, 2H), 2.29−2.20 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 195.5, 152.1, 151.9, 135.7, 125.9, 125.2, 124.8, 121.7, 117.9, 115.2, 54.3, 38.0, 25.7, 23.3. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 1743, 1655, 1556, 1143, 758. MS (ESI): m/z = 244 (100) [$(M + H)^+$]. HRMS (ESI): calcd for $C_{14}H_{14}NO_3$ [$(M + H)^+$] = 244.0974, found = 244.0968.

*Methyl 4a-Hydroxy-4-oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**11a**).* To a solution of **8a** (50 mg, 0.20 mmol, 1.0 equiv) in THF (20 mL/mmol) was added 0.1 M aqueous sodium hydroxide (410 μL, 0.02 mmol, 20 mol %), and the reaction mixture was stirred under air (balloon) at room temperature for 18 h.

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After completion of the reaction as indicated by thin-layer chromatography (pentane/EtOAc 7:3) [UV], the reaction was diluted with water (20 mL) and extracted by ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous sodium sulfate, and evaporated to obtain a residue. Column chromatographic purification (dry loading, pentane/EtOAc 1:1) [UV] afforded compound **11a**. White solid (38 mg, 75%), mp 111−113 °C. TLC: R_f = 0.22 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96−7.57 (m, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.05−7.00 (m, 1H), 6.99−6.96 (m, 1H), 4.57 (br, 1H), 4.50 (s, 1H), 3.86 (br, 3H), 2.55 (dt, J = 17.2, 6.7 Hz, 1H), 2.37 (dt, J = 17.2, 6.7 Hz, 1H), 2.10−2.04 (m, 1H), 1.89−1.64 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 209.3, 152.9, 131.2, 130.2, 123.6, 123.4, 116.1, 110.1, 82.2, 69.3, 52.9, 37.0, 29.2, 18.7. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3412, 2972, 1713, 1682, 1474, 1448, 1392, 1055, 770. MS (ESI): m/z = 547 (40) [(2M − OH + H + MeCN)$^+$], 506 (100) [(2M − OH + H)$^+$], 244 (20) [(M − OH)$^+$]. HRMS (ESI): calcd for $C_{14}H_{14}NO_3$ [(M − OH)$^+$] = 244.0974, found = 244.0968. The structure of this compound was also confirmed by single-crystal XRD analysis (CCDC 1877643).

*Methyl 4-Hydroxy-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**12a**).* To a solution of **8a** (50 mg, 0.20 mmol, 1.0 equiv) in MeOH (20 mL/mmol) was added sodium borohydride (8.50 mg, 0.22 mmol, 1.1 equiv) at −78 °C. After 1 h of stirring, the temperature was allowed to rise to room temperature and the reaction mixture stirred for another 16 h. After completion of the reaction as indicated by thin-layer chromatography (pentane/EtOAc 1:1) [UV], the reaction was diluted with water (20 mL) and extracted by EtOAc (2 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous sodium sulfate, and evaporated to obtain residue. Column chromatographic purification (wet loading with 1 mL DCM, pentane/EtOAc 1:1) [UV] afforded compound **12a** as an oil (47 mg, 93%). TLC: R_f = 0.15 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85−7.52 (m, 2H), 7.21−7.18 (m, 1H), 6.97 (td, J = 7.4, 0.9 Hz, 1H), 4.43−4.42 (m, 1H), 4.22−4.18 (m, 1H), 3.83 (s, 3H), 3.75 (t, J = 6.6 Hz, 1H), 2.04−1.90 (m, 2H), 1.83−1.78 (m, 1H), 1.70−1.64 (m, 1H), 1.59−1.51 (m, 1H), 1.34−1.17 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.4, 142.1, 131.5, 127.7, 126.3, 123.0, 115.6, 70.7, 60.7, 52.6, 46.1, 29.5, 26.0, 19.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3427, 2940, 2860, 1686, 1441, 1386, 1083, 753. MS (ESI): m/z = 248 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{14}H_{18}NO_3$ [(M + H)$^+$] = 248.1287, found = 248.1281.

*Methyl 4-Ethyl-4-hydroxy-1,2,3,4,4a,9a-hexahydro-9H-carbazole-9-carboxylate (**13a**).* To a solution of **8a** (50 mg, 0.20 mmol, 1.0 equiv) in Et_2O (20 mL/mmol) was added ethylmagnesium bromide (1 M in THF, 265 μL, 0.27 mmol, 1.3 equiv) at −20 °C. After 1 h of stirring, the temperature was allowed to rise to room temperature and the reaction stirred for another 16 h. After completion of the reaction as indicated by thin-layer chromatography (pentane/EtOAc 3:1) [UV], the reaction was diluted with water (20 mL) and extracted by EtOAc (2 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous sodium sulfate, and evaporated to obtain residue. Column chromatographic purification (wet loading with 1 mL DCM, pentane/EtOAc 2:1) [UV] afforded compound **13a**. White solid (35 mg, 70%), mp 88−90 °C. TLC: R_f = 0.40 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.94−7.92 (m, 1H), 7.69 (br, 1H), 7.15−7.12 (m, 1H), 6.94−6.91 (m, 1H), 4.43−4.38 (m, 1H), 3.78 (s, 3H), 3.74 (s, 1H), 3.42 (d, J = 7.3 Hz, 1H), 1.98−1.95 (m, 1H), 1.85−1.78 (m, 1H), 1.71−1.64 (m, 2H), 1.56−1.50 (m, 2H), 1.40−1.29 (m, 1H), 1.12−1.03 (m, 1H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6): δ 152.6, 141.9, 132.8, 126.8, 126.6, 122.2, 114.7, 72.9, 60.2, 51.5, 50.2, 32.8, 31.1, 26.0, 19.2, 6.0. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3460, 2937, 2867, 1683, 1476, 1441, 1263, 1141, 1087, 753. MS (ESI): m/z = 313 (80) [(M + 2NH_4 + 2H)$^+$], 295 (100) [(M + NH_4 + 2H)$^+$]. HRMS (ESI): calcd for $C_{16}H_{22}NO_3$ [(M + H)$^+$] = 276.1600, found = 276.1595.

*Methyl 4a-Methyl-4-oxo-1,2,3,4,4a,9a-cis-hexahydro-9H-carbazole-9-carboxylate (**14a**).* To a solution of **8a** (50 mg, 0.20 mmol, 1.0 equiv) in THF (20 mL/mmol) was added sodium hydride (60% on mineral oil, 9 mg, 0.22 mmol, 1.1 equiv) at 0 °C. After 15 min, MeI (14 μL, 0.22 mmol, 1.1 equiv) was added, the temperature was allowed to rise to room temperature, the reaction was stirred for 2 h. After completion of the reaction as indicated by thin-layer chromatography (pentane/EtOAc 4:1) [UV], the reaction was diluted with water (20 mL) and extracted by EtOAc (2 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous sodium sulfate, and evaporated to obtain residue. Column chromatographic purification (wet loading with 1 mL DCM, pentane/EtOAc 1:1) [UV] afforded compound **14a** as an oil (37 mg, 70%). TLC: R_f = 0.33 (pentane/EtOAc 4:1) [UV]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (br, 1H), 7.26−7.22 (m, 1H), 7.00−6.95 (m, 2H), 4.38 (br, 1H), 3.88 (s, 3H), 2.45−2.38 (m, 1H), 2.35−2.27 (m, 1H), 2.09−2.02 (m, 1H), 1.85−1.74 (m, 2H), 1.69−1.60 (m, 1H), 1.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 209.9, 153.4, 141.1, 133.8, 129.0, 123.5, 123.3, 115.5, 69.0, 56.3, 52.8, 38.5, 28.5, 25.3, 18.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2954, 1699, 1479, 1439, 1387, 1287, 1087, 753. MS (ESI): m/z = 260 (100) [(M + H)$^+$]. HRMS (ESI): calcd for $C_{15}H_{18}NO_3$ [(M + H)$^+$] = 260.1287, found = 260.1281.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b03144.

^{1}H and ^{13}C{^{1}H} NMR spectra for all compounds, UV/vis spectra of compounds **1a**, **6a**, and **6i**, details for SC-XRD determination of compound **8a** and **11a**, and computational chemistry details (PDF)

X-ray data for compound **8a** (CIF)

X-ray data for compound **11a** (CIF)

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Notes

The authors declare no competing financial interest.

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