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Enantioselective photocyclisation reactions of 2-aryloxy-

cyclohex-2-enones mediated by a chiral copper-bisoxazoline

complex

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ABSTRACT

The photocyclisation of the title compounds leads upon direct irradiation at $\lambda = 366$ nm in dichloromethane solution to racemic *cis*-2,3,4a,9b-tetrahydro-1*H*-dibenzofuran-4-ones (nine examples, 37-74% yield). Since it was found that the substrates show a significant bathochromic absorption shift upon treatment with EtAlCl₂, it was attempted to perform the reactions enantioselectively in the presence of a chiral Lewis acid. A complex of Cu(ClO₄)₂·6 H₂O and a bisoxazoline ligand gave the best enantioselectivities (up to 60% *ee*). Two procedures are reported for the enantioselective photocyclisation. The first protocol is based on a direct irradiation at $\lambda = 368$ nm (LED) with a catalyst loading of 50 mol% and it delivered the products in 26-76% yield with 22-40% *ee*. The second protocol is applicable to electron rich 2-aryloxycyclohex-2-enones (31-62% yield, 29-46% *ee*) and relies on sensitization by thioxanthone (50 mol%) at $\lambda = 419$ nm.

Keywords

Bisoxazoline ligand Cu catalysis Enantioselectivity Photochemistry Photocyclisation Sensitization **Graphical Abstract** Cu(ClO₄)₂·6 H₂O R Rn r.t. (CH₂Cl₂) 26-76% up to 60% ee Conditions: hv (λ = 368 nm) or hv (λ = 419 nm), 50 mol% thioxanthone

Introduction

In 1975, Schultz and Lucci reported on the first photocyclisation reaction of 2-aryloxycyclohex-2-enones.¹ Upon irradiation of substrate **1a** for 23 hours in a solvent mixture of benzene, methanol, and acidic acid, dihydrofuran *rac*-**3a** was formed (Scheme 1) and the compound was isolated after re-crystallization in analytically pure form (80% yield). The photolysis was

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performed in pyrex glass which served as filter to cut-off short wavelength irradiation below $\lambda = 280$ nm. Still, a further conversion of the product was notable upon prolonged irradiation and minor side products were isolated. The reaction was explored with a variety of different substrates in the context of natural product synthesis as it promised an efficient access to the morphine skeleton.^{2,3}

SCHEME 1. Proposed reaction pathway for the photocyclisation of 2-phenyloxycyclohex-2-enone



1a to product rac-3a

Mechanistic evidence suggested that the photocyclisation proceeds via a carbonyl ylide, e.g. *rac*-**2a**, which is the formal product of a conrotatory ring closure. Dittami et al. trapped intermediates of this type by an intramolecular 1,3-dipolar cycloaddition and established the relative configuration of the products.⁴ To account for the relative *cis*-configuration of the photocyclisation products (cf. *rac*-**3a**), it was assumed that protonation of the carbonyl ylides occurs by the solvent and this notion was supported by deuteration experiments.^{2a} Flash photolysis studies by Wolff revealed that the reaction proceeds via the excited triplet state of the aryloxyenone (**1a***) but it was not possible to resolve the adiabatic reaction step from this state to the triplet state of the carbonyl ylide.⁵ Additional evidence for the intermediacy of triplet aryloxyenones was obtained from sensitization experiments and oxygen quenching studies.

We became interested in the formal $[6\pi]$ -photocyclisation^{6,7} of 2-aryloxycyclohex-2-enones⁸ in the context of our work⁹ on Lewis-acid catalyzed enantioselective photochemical reactions.¹⁰ It was found that Lewis acid coordination¹¹ to cyclic alkenones leads to a bathochromic shift of the intense ($\varepsilon \approx 15000 \text{ M}^{-1} \text{ cm}^{-1}$) $\pi\pi^*$ absorption. Due to this shift, the strong absorption of the Lewis acid complex overlaps the weak ($\varepsilon \le 100 \text{ M}^{-1} \text{ cm}^{-1}$) n π^* absorption of the non-coordinated enone, which is responsible for the [2+2] photocycloaddition chemistry of this class of compounds. If irradiated at a suitable wavelength, only the Lewis acid complex is photochemically excited due to its higher absorption cross-section and subsequent reactions can proceed enantioselectively if a chiral Lewis acid is used.¹² We speculated that compounds like aryloxyenone **1a** might show a similar behavior and might potentially undergo enantioselective photocyclisation reactions in the presence of a chiral Lewis acid.¹³ Preliminary UV-Vis spectra (Figure 1) suggested that the plan could be viable as compound **1a** exhibited a significant bathochromic shift upon addition of EtAlCl₂ as the Lewis acid.



FIGURE 1. UV-Vis spectra of compound 1a in the presence of various amounts of EtAlCl₂.

The strong absorption with maxima at $\lambda = 223$ nm ($\epsilon = 11450 \text{ M}^{-1} \text{ cm}^{-1}$) and at $\lambda = 241$ nm ($\epsilon = 10460 \text{ M}^{-1} \text{ cm}^{-1}$) vanished upon Lewis acid addition and a new band appeared with a maximum

at $\lambda = 292 \text{ nm} (\varepsilon = 10840 \text{ M}^{-1} \text{ cm}^{-1})$. The strong band stretches into a wavelength region, in which the weak $n\pi^*$ absorption of the uncomplexed enone **1a** occurs ($\lambda = 320 \text{ nm}$, $\varepsilon = 114 \text{ M}^{-1} \text{ cm}^{-1}$). Based on this result we started to search for chelating chiral Lewis acids which would enable an enantioselective photocyclisation reaction of 2-aryloxycyclohex-2-enones. The results of our experiments are summarized in this report.

RESULTS

Preparation of the starting materials and photocyclisation to racemic products. The synthesis of the photochemical substrates was performed in analogy to the procedure of Schultz and co-workers.^{1,2a} Isophorone oxide (*rac*-4)¹⁴ served as the starting material and underwent a potassium hydride-assisted ring opening/elimination sequence. A dipolar aprotic solvent additive is required in this step and *N*,*N*-dimethylpropyleneurea (DMPU) was found to be a suitable alternative to the toxic hexamethylphosphoramide. In addition, we found that DMSO was a superior solvent as compared to THF, in particular if electron-deficient phenols (HOAr) were used as oxygen nucleophiles (Table 1, entries 5-7). Yields were not further optimized as sufficient starting material for the subsequent photochemical reaction could be readily secured. Since we planned to perform all catalytic experiments in dichloromethane solution, the racemic reactions were also run in this solvent. Employing fluorescent lamps,¹⁵ we found an optimum yield at a wavelength of $\lambda = 366$ nm for the reaction $\mathbf{1a} \rightarrow rac - \mathbf{3a}$ (Table 1, entry 1). At $\lambda = 300$ nm and $\lambda = 350$ nm, the yields were lower (35% and 68%, respectively) while no reaction was observed at $\lambda = 419$ nm.¹⁶

Table 1. Formation of substrates 1 by epoxide ring opening/elimination from isophorone oxide (*rac*-4) and subsequent photocyclisation to racemic products *rac*-3



^a Yield of isolated product **1**. ^b Reaction time until full conversion was reached. ^c Yield of isolated product *rac*-**3a**. ^d The reaction was performed in THF as the solvent. ^e The yield was 81% at c = 20 mM.

The high yield achieved for product *rac*-**3a** could not be reproduced for all other substrates but again it was not attempted to optimize the procedure. In general, reactions were performed at a concentration of c = 10 mM under deaerated conditions and were stopped if no starting material

could be detected by TLC. The relative configuration of the products rac-3 was assigned based on the reported NMR shift data of known compounds of this class. The constitution of product rac-3i (C-C bond formation at carbon atom C1 of the naphthalene) had been previously established⁵ and was confirmed.

SCHEME 2. Influence of the water content of the solvent on the relative configuration of



photocyclisation products from substrate 1a

As mentioned above, the *cis* configuration is assumed to be the result of the *inter*molecular protonation of the intermediate carbonyl ylide. Scheme 2 illustrates the results obtained by irradiation with a light-emitting diode (LED) at $\lambda = 368 \text{ nm}^{17}$ in dichloromethane solutions with varying water contents. If distilled dichloromethane was used which was not further dried the only product was *cis*-product *rac*-**3a**. Under strictly anhydrous conditions, *trans*-diastereoisomer *rac*-**5a** was obtained as the major product that was configurationally stable upon chromatography. Its formation can be explained by an *intra*molecular suprafacial 1,4-hydrogen shift to occur in carbonyl ylide *rac*-**2a** (cf. Scheme 1). When treated with base (e.g. K₂CO₃ in wet CH₂Cl₂), compound *rac*-**5a** was quantitatively transformed into *cis*-diastereoisomer *rac*-**3a**.

Search for an appropriate chiral Lewis acid. Substrate 1a exhibits two Lewis basic oxygen atoms which could potentially form a five-membered chelate complex with an appropriate Lewis acid. Consequently, the use of a chiral chelating Lewis acid with a C_2 -symmetric ligand seemed to be a good starting point to identify suitable catalysts to promote the reaction of 1a to product 3a enantioselectively.

Table 2. Ratio of enantiomers as observed in the $Cu(OTf)_2$ -promoted photocyclisation $1a \rightarrow 3a/ent-3a$: Influence of the chiral ligand



^a The reaction was run to completion (20-24 h reaction time) unless indicated otherweise. ^b Yield of isolated product. ^cThe enantiomric ratio (e.r.) was determined by chiral HPLC analysis. ^d The enantiomeric excess (*ee*) was calculated from the e.r.. ^e 50% conversion after 24h. ^f65% conversion after 24 h.

The ligand screen was performed with $Cu(OTf)_2^{18}$ and chiral oxazoline ligands¹⁹ in deaerated dichloromethane solution and a few selected results are summarized in Table 2. As expected from previous work⁹ the presence of a Lewis acid did not lead to a rate acceleration but rather did the reaction rate decrease. The only meaningful enantioselectivities were recorded with bidentate bisoxazoline $(box)^{20}$ ligands **6a-6d** derived from 2,2-dimethylmalonic acid (entries 1-4). An asymmetric induction by the other ligands **6e-6g** (entries 5-7) could not be detected and racemic product *rac*-**3a** was obtained. Among the box ligands, the respective dibenzylated ligand **6c** was the superior choice although the enantioselectivity was far from optimal (20% *ee*, entry 3). A more electron rich benzyl group (PBB = para-benzyloxybenzyl, ligand **6d**, entry 4) delivered a lower enantiomeric excess (*ee*). Although the absolute configuration at the stereogenic centers of ligands **6b** and **6c** were identical the preference for one product enantiomer was opposite (entries 2 and 3, *vide infra*).

With box ligand **6c** providing the highest enantioselectivity in the screening, this ligand was used in combination with different metal salts (see Supplementary Material). Typical conditions (see Table 2) included the use of 0.5 equiv. of the metal salt and 0.6 equiv. of ligand **6c** in CH₂Cl₂ solution (c = 10 mM, $\lambda = 366$ nm, t = 24 h). Among the various metal salts, there was only a single beneficial effect to be observed when Cu(ClO₄)₂·6 H₂O was employed as the source of the copper ion. Although the conversion was even slower (31% yield after 24 h) than with Cu(OTf)₂, the enantiomeric excess doubled to 40% *ee*. Since these reactions were performed at room temperature it was hoped that a lower reaction temperature might lead to an improved enantioselectivity. Disappointingly, the photocyclisation did not proceed at -65 °C and was sluggish at 0 °C. A lower catalyst loading led to a decreased enantioselectivity if the reaction was performed at ambient temperature. If the amount of Cu(ClO₄)₂·6 H₂O was increased from 0.5 to 1.0 equivalents, the yield increased but the enantioselectivity decreased (53%, 36% *ee*). If the

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ligand loading was increased to 1.0 equiv. and the loading of $Cu(ClO_4)_2 \cdot 6 H_2O$ was kept at 0.5 equiv. there was a significant increase in enantioselectivity but the yield did not improve (34%, 60% *ee*).

Screening with various substrates and absolute configuration. Two light sources which emit at 366 and 368 nm, respectively, were evaluated to perform the enantioselective reactions with all available substrates (Table 3). The 366 nm light source consists of a set of 16 fluorescent lamps with a broad emission spectrum and with a significant heat evolution.¹⁵ The 368 nm light source is a LED with a narrow emission spectrum, which is immersed in a flask²¹ and which evolves no heat. Reactions with the latter light source turned out to be more reproducible at ambient temperature. In addition, the reaction with parent substrate 1a was faster and higher yielding with the LED than with the fluorescent lamp. Under standard conditions (Table 2, entry 1), the yield was 53% as compared to 31% while the enantioselectivity remained identical (40% ee). Donor substitution in *para*-position of the aryl group was inconsequential to the enantioselectivity (entries 2-4) while acceptor substitution led to a decrease in enantioselectivity (entries 5-7). The relatively high yields in the reactions of compounds 1e, 1g, and 1h (entries 5, 7, 8) indicate that racemic background reactions which occur upon direct excitation are significant. The naphthyloxy-substituted substrate 1i gave product 3i in a modest yield and with low enantioselectivity (entry 9). In general, there was no substrate 1b-1i which showed a better performance than parent compound 1a. Yields of isolated products 3 remained on average moderate and varied between 26-76%. The enantioselectivity was also variable and ee values between 22% and 40% ee were recorded. All products were levorotatory indicating that their absolute configuration was identical irrespective of the aromatic substituent.

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^a All reactions were performed on a scale of 0.1 mmol (c= 10 mM) with a LED lamp (3 W power output)¹⁷ as the light source. ^b Irradiation time. ^c Yield of recovered starting material. ^d Yield of isolated product. ^e The enantiomeric excess (*ee*) was determined by chiral HPLC analysis.

The absolute configuration of the major enantiomer in the reaction $1h \rightarrow 3h$ could be elucidated by anomalous X-ray diffraction (Figure 2). In order to obtain a configurationally homogenous sample the *ee* of the compound was enriched by chiral semipreparative HPLC to >99%. The identity of the enantiomer, of which the crystal structure was determined, was confirmed by subsequent HPLC analysis.



FIGURE 2. Absolute configuration of product **3h** as determined by anomalous X-ray diffraction.

As in the solid-state reaction of 2-arylthiocyclohex-2-enones,⁸ the enantioface differentiation in the current photocyclisation reaction is likely due to a helical conformation. In the present case the helicity must be induced by the chiral Cu complex. Attack at the β -carbon atom of the enone occurs from the respective *Re* face as depicted for substrate **1a** in Figure 3.



FIGURE 3. Twisted conformation **1a**' of substrate **1a**, possible coordination of **1a** to the Cu bisoxazoline complex Cu(ClO₄)₂·**6c**, and structure of Cu(H₂O)₂(SbF₆)₂·**6a**

Coordination of compound **1a** to the Cu^{II} bisoxazoline complex is expected to occur in a more or less square-planar fashion with the two Lewis-basic oxygen atoms of the substrate binding to the central metal atom. However, it is known that the oxygen atoms and the nitrogen atoms of the bisoxazoline ligand are not located in a single plane but that the square planar arrangement is somewhat distorted.²² X-Ray crystallographic data for the complex $Cu(H_2O)_2(SbF_6)_2$. 6a for example revealed that there is a positive dihedral angle between the marked atoms O^{1} -Cu-N¹-C¹ of ca. +30 $^{\circ}$.^{22a} A similar dihedral angle is observed for O²-Cu-N²-C² leading to a twist in the coordination of the water atoms with one water molecule positioned below but the other positioned above the plane. If one assumes that the oxygen atoms of compound **1a** follow the same binding pattern as the oxygen atoms of the water molecules, it can be readily explained why conformation 1a' is preferred and why enantiomer 3a is the major product of the photocyclisation. Moreover, the hypothesis also explains the reversal of enantioselectivity with ligand **6b**. In the Cu(H₂O)₂(SbF₆)₂·**6b** the above-mentioned dihedral angles are negative^{21,22b} inducing a twist of substrate 1a in the opposite direction with the Si face now being more readily accessible. Another aspect deserves to be mentioned. If one assumes an initial coordination as shown in Figure 3, the ether oxygen atom of the substrate will progressively decomplex from the copper center when approaching the transition state to the ylide intermediate 2a (Scheme 1). Among other factors (vide supra), the insufficient chelation may be a reason for the only moderate enantioselectivity of the photocyclisation.

Reaction mechanism and visible-light induced photocyclisation in the presence of a sensitizer. Although it was established earlier that the photocyclisation of substrates **1** proceeds via a triplet intermediate,⁵ it was not clear whether the Cu-catalyzed reaction was also a triplet process. Preliminary experiments with O_2 as putative quencher of a triplet intermediate revealed that the photocyclisation of **1a** was indeed slower than under exclusion of oxygen (see Supplementary Data) but the rate decrease was less significant than observed for the non-catalyzed reaction.⁵ When irradiating a substrate with options for competing pathways, i.e. photocyclisation vs. [2+2] photocycloaddition, it had been previously found^{4c} that the photocycloaddition which is a fast triplet process²³ prevails. In the present study, 2-phenyloxyenones **7** were compared under the conditions of the Cu-catalyzed process and it was found that substrate **7a** (R = Me) expectedly yields the photocyclisation product **8** (Scheme 3). The enantioselectivity determination suffered from insufficient baseline separation but the determined *ee* was in the range which was previously observed for products **3**. Product **8** was also levorotatory. Substrate **7b** (R = pent-4-enyl) gave upon irradiation under the Cu-catalyzed conditions almost exclusively the [2+2] photocycloaddition product *rac*-**9**. The same observation has been previously made upon direct excitation of **7b**.^{4c} The results illustrate that the [2+2] photocycloaddition is significantly faster than the photocyclisation and it adds another piece of evidence that also the Cu-promoted reaction proceeds via the aryloxyenone triplet state.





In a final set of experiments it was probed whether the excitation of enones **1** could be achieved by sensitization. Thioxanthone (TXT) seemed a suitable sensitizer which would allow the reaction to be performed with visible light. Gratifyingly, it was found that the addition of 50 mol% of the sensitizer enabled a conversion of several substrates upon irradiation at $\lambda = 419$ nm for 24 hours (Table 4). Complete reactions were found for substrates **1a**, **1d**, **1h**, and **1i** (39-62% yield, entries 1, 4, 8, and 9). Aryloxyenones **1e-1g** with an electron deficient aryl group showed a very slow conversion (entries 5-7). The reaction did not proceed or remained incomplete after 24 h. Presumably, the triplet energy of the sensitizer²⁴ is too low to promote these substrates into the excited state. Notable enantioselectivites (46% and 47% *ee*) were observed in two cases (entries 3 and 6).

Table 4. Cu-Mediated enantioselective photocyclisation of 2-aryloxy¬cyclohex-2-enones 1 to products 3 upon sensitized excitation at $\lambda = 419$ nm

50 m 60 m 1	h∨ (λ = 419 r hol% Cu(ClO ₄ hol% 6c , 50 m r.t. (CH ₂ Cl ₂	nm))₂·6 H₂O ol% TXT ₂) ►			Y.	3
entry ^a	product	r.s.m. ^b	yield ^c	<i>ee</i> ^d [%]		
		[%]	[%]			
1	3a	—	57	30		
2	3b	19	31	35		
3	3c	32	32	46		
4	3d	_	62	29		
5	3e	23	-11	27		
6	3f	66	17	47		
7	3g	75	e	×		
8	3h	-	39	30		
9	3i	(-	57	9	_	
					-	

^a All reactions were performed on a scale of 0.1 mmol (c= 10 mM) with a set of fluorescence lamps (RPR-4190 Å)^{15d} as the light source. The reaction time was in all cases 24 hours. ^b Yield of recovered starting material. ^c Yield of isolated product. ^d The enantiomeric excess (*ee*) was determined by chiral HPLC analysis. ^e No reaction product could be isolated.

CONCLUSION

In summary, we have discovered the first enantioselective photocyclisation reactions of 2aryloxycyclohex-2-enones in solution and we have proven that a chiral Lewis acid approach is applicable to this reaction class. A complex of $Cu(ClO_4)_2 \cdot 6 H_2O$ and bisoxazoline ligand 6c was employed as the Lewis acid in most of the reported transformations. Evidence was collected that the Cu-promoted reactions follow – like the uncatalyzed reactions – a triplet mechanism. In the dynamic catalyst-substrate system there is an equilibrium between the non-complexed substrate and the substrate in the complex. For the non-complexed substrate excitation occurs at long wavelength via its weak $n\pi^*$ absorption, e.g. for **1a** at $\lambda = 320$ nm ($\epsilon = 114$ M⁻¹ cm⁻¹). The longwavelength absorption of the Lewis acid complex has $\pi\pi^*$ character. Upon direct excitation, the fact that population of the $\pi\pi^*$ triplet state can only occur via the $\pi\pi^*$ singlet state hampers the catalysis because intersystem crossing (ISC) is likely slow.²⁵ This issue was already discussed in the context of enantioselective Lewis-acid promoted [2+2] photocycloaddition reactions.²⁶ The uncatalyzed reaction can proceed via rapid ISC from the $n\pi^*$ singlet state and thus acts as a significant racemic background reaction.²⁷ Upon sensitization, the chosen triplet sensitizer apparently does not allow for a perfect discrimination between complexed and non-complexed substrate. As a result, the racemic background reaction remains viable and dilutes the asymmetric induction of the chiral Lewis acid. Based on this analysis, it should be possible to further improve the enantioselectivity by judicious choice of the sensitizer. Promising results along these lines have been recently achieved by the Yoon group in the context of [2+2] photocycloaddition reactions.12b

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EXPERIMENTAL SECTION

General Methods:

All reactions sensitive to air or moisture were carried out in flame-dried glassware under a positive pressure of argon using standard Schlenk techniques. Dry tetrahydrofuran (THF) and dichloromethane (CH₂Cl₂) were obtained from an MBRAUN MB-SPS 800 solvent purification system. Other dry solvents and chemicals were obtained from commercial suppliers in the highest purity available and were used without further purification. Technical solvents used for aqueous workup and for column chromatography [n-pentane (pentane), ethyl acetate (EtOAc), diethyl ether (Et₂O), dichloromethane (CH₂Cl₂), methanol (MeOH)] were distilled prior to use. The following compounds were prepared according to published procedures: rac-4,¹⁴ 6a,^{22a} 6b,²⁸ 6c,²⁹ **6e**.³⁰ Photochemical experiments at $\lambda = 366$ nm and $\lambda = 419$ nm were performed in *Duran* tubes (volume 10 mL) in an RPR-100 photochemical reactor (Southern New England Ultra Violet Company, Branford, CT, USA) equipped with fluorescence lamps ($\lambda = 366$ nm, $\lambda = 419$ nm).¹⁵ Photochemical experiments using a LED ($\lambda = 368 \text{ nm}$)¹⁷ were carried out in a Schlenk tube (diameter = 1 cm) with a polished quartz rod as an optical light guide, which was roughened by sandblasting at one end.²¹ The roughed end has to be completely submerged in the solvent during the reaction, in order to guarantee optimal and reproducible irradiation conditions. Prior to irradiation, the dichloromethane was deoxygenated by purging with argon in an ultrasonicating bath for 15 minutes. Column chromatography was performed on silica gel 60 (Merck, 230-240 mesh) with the eluent mixtures given for the corresponding procedures. Thin-layer Chromatography (TLC) was performed on silica-coated glass plates (silica gel 60 F 254). Compounds were detected by UV ($\lambda = 254$ nm, 366 nm), KMnO₄ and CAM solution (cerium) ammonium molybdate). Analytical HPLC was performed using a chiral stationary phase (Daicel ChiralCell, Chemical Industries, flow rate: 1.0 mL/min, type and eluent is given for the

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corresponding compounds) and UV detection ($\lambda = 210$ nm or 254 nm) at 20 °C. IR spectra were recorded on a JASCO IR-4100 (ATR) or a Perkin Elmer Frontier IR-FTR spectrometer by ATR technique. The signal intensity is assigned using the following abbreviations: s (strong), m (medium), w (weak). MS and HRMS measurements were performed on a Thermo Scientific DFS instrument (EI) or a Thermo Scientific LTQ-FT Ultra (ESI). ¹H and ¹³C spectra were recorded at 300 K either on a Bruker AV-360, a Bruker AVHD-400, or a Bruker AVHD-500 spectrometer. Chemical shifts are reported as parts per million (ppm) relative to chloroform [δ (¹H) = 7.26 ppm, δ (¹³C) = 77.16 ppm]. All coupling constants (*J*) are reported in Hertz (Hz). The relative configuration of chiral products and the multiplicity of the ¹³C-NMR signals were determined by two-dimensional NMR experiments (COSY, NOESY, HSQC, HMBC). X-ray crystallography was performed on a Bruker D8 Venture Duo IMS system equipped with a Helios optic monochromator and a Mo IMS microsource ($\lambda = 0.71073$ Å). The data was analyzed using a Bruker SAINT software package using a narrow-frame algorithm. UV/Vis spectra were recorded on a Perkin Elmer Lambda 35 UV/Vis spektometer using a Hellma precision cell made of quartz SUPRASIL[®] with a pathway of 1 mm. Optical rotations were determined using a Bellingham+Stanley ADP440+ polarimeter.

General procedure for the synthesis of the irradiation precursor. To a solution of the appropriate phenol (1.0 equiv.) in dry DMSO (0.3 mL/mmol), KH in mineral oil (30%, 0.1 equiv.) was added and the mixture was stirred at room temperature for 10 min. After addition of isophorone oxide¹⁴ (*rac*-4, 1.05 equiv.), DMPU (0.82 equiv.) was added. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the solution was extracted three times with Et₂O (5 mL/mmol). The combined organic layers were washed with brine (10

mL/mmol), dried over Na₂SO₄ and filtered. After evaporation the crude material was purified by column chromatography.

2-(4-*tert***-Butylphenoxy)-3,5,5-trimethyl-2-cyclohexen-1-one (1c).** According to the general procedure, compound **1c** was synthesized starting from 4-*tert*-butylphenol (925 mg, 6.16 mmol, 1.0 equiv.). Purification by column chromatography (pentane/Et₂O 10:1, UV, CAM) gave the product as a light yellow solid (1.46 g, 5.10 mmol, 83%). m.p.: 98 °C. TLC: R_f = 0.54 (pentane/Et₂O 2:1) [UV, CAM]. IR (ATR): \tilde{v} (cm⁻¹) = 2954 (m, C-H), 1676 (C=O), 1508 (s), 1230 (s), 1181 (s), 835 (s), 827 (s). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.14 [s, 6H, C(CH₃)₂], 1.28 [s, 9H, C(CH₃)₃], 1.89 (s, 3H, CH₃), 2.41 (s, 2H, H-6), 2.42 (s, 2H, H-4), 6.74-6.77 (m, 2H, H_{ar}), 7.24-7.27 (m, 2H, H_{ar}). ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 18.3 (q, CH₃), 28.6 [q, C(CH₃)₂], 31.7 [q, C(CH₃)₃], 33.4 (s, C-5), 34.2 [s, C(CH₃)₃], 45.8 (t, C-4), 52.1 (t, C-6), 114.3 (d, C_{ar}), 126.5 (d, C_{ar}), 143.9 (s, C'Bu), 144.4 (s, C=C), 145.9 (s, C=C), 155.5 (s, C_{ar}), 193.2 (s, C-1). MS (EI, 70 EV): m/z (%) = 150 (16), 135 (100), 107 (28). HRMS (EI, 70 eV): Calculated for C₁₉H₂₆O₂ [M⁺] = 286.1927. Found = 286.1925.

2-(4-Cyanophenoxy)-3,5,5-trimethyl-2-cyclohexen-1-one (**1g**). According to the general procedure, compound **1g** was synthesized starting from 4-cyanophenol (734 mg, 6.16 mmol, 1.0 equiv.) Purification by column chromatography (pentane/Et₂O 3:2, UV, CAM) gave the product as a light yellow solid (965 mg, 3.78 mmol, 61%). m.p.: 62 °C. TLC: R_f = 0.60 (pentane/Et₂O 1:2) [UV, CAM]. IR (ATR): \tilde{v} (cm⁻¹) = 3270 (m), 2957 (w, C-H), 2231 (s, CN), 1674 (s, C=O), 1602 (s, C=C), 1505 (s), 1239 (s), 1166 (s), 836 (s, C-H). ¹H NMR (360 MHz, CDCl₃): δ (ppm) = 1.15 [s, 6H, C(CH₃)₂], 1.89 (s, 3H, CH₃), 2.42 (s, 2H, H-6), 2.45 (s, 2H, H-4), 6.88 (d, *J* = 8.1 Hz, 2H, H_{ar}), 7.56 (d, *J* = 8.1 Hz, 2H, H_{ar}). ¹³C {¹H} NMR (90 MHz, CDCl₃): δ

 $(ppm) = 18.2 [q, C(CH_3)_2], 28.6 (q, CH_3), 33.4 (s, C-5), 45.7 (t, C-4), 51.8 (t, C-6), 105.4 (s, C_{ar}), 115.9 (d, C_{ar}), 119.1 (s, CN), 134.3 (d, C_{ar}), 143.1 (s, C=C), 146.7 (s, C=C), 161.1 (s, C_{ar}), 192.1 (s, C-1). MS (EI, 70 eV): <math>m/z$ (%) = 256 (100) [M⁺], 240 (13) [(M-CH_3)⁺], 227 (28), 199 (35), 143 (24), 130 (36), 109 (35), 69 (84). HRMS (EI): Calculated for C₁₆H₁₇NO₂ [M⁺] = 255.1258. Found = 255.1254.

2-(4-Bromophenoxy)-3,5,5-trimethyl-2-cyclohexen-1-one (1h). According to the general procedure, compound **1h** was synthesized starting from 4-bromophenol (533 mg, 3.08 mmol, 1.0 equiv.). Purification by column chromatography (pentane/Et₂O 10:1, UV, CAM) gave the product as a yellow solid (832 mg, 2.69 mmol, 87%). m.p.: 46 °C. TLC: $R_f = 0.60$ (pentane/Et₂O 2:1) [UV, CAM]. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2957 (m, C-H), 1668 (s, C=C), 1479 (s), 1227 (s), 823 (s). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.14 [s, 6H, C(CH₃)₂], 1.88 (s, 3H, CH₃), 2.40 (s, 2H, H-6), 2.43 (s, 2H, H-4), 6.67-6.73 (m, 2H, H_{ar}), 7.31-7.35 (m, 2H, H_{ar}). ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 18.2 (q, CH₃), 28.6 [q, C(CH₃)₂], 33.4 (s, C-5), 45.8 (t, C-4), 51.9 (t, C-6), 114.1 (s, C-10), 116.8 (d, C-8), 132.5 (d, C-9), 143.6 (s, C=C), 146.3 (s, C=C), 156.9 (s, C-7), 192.7 (s, C-1). MS (EI, 70 eV): m/z (%) = 308 (46) [M⁺], 280 (8), 183 (15), 172 (100), 93 (31), 62 (20). HRMS (EI, 70 eV): Calculated for C₁₅H₁₇O₂⁷⁹Br [M⁺] = 308.0414. Found = 308.0406. Calculated for C₁₅H₁₇O₂⁸¹Br [M⁺] = 310.0386. Found = 310.0393.

2-(2-Naphthoxy)-3,5,5-trimethyl-2-cyclohexen-1-one (1i). According to the general procedure, compound 1i was synthesized starting from 2-naphthol (444 mg, 3.08 mmol, 1.0 equiv.). Purification by column chromatography (pentane/Et₂O 10:1, UV, CAM) gave the product as a light yellow solid (695 mg, 2.48 mmol, 80%). m.p.: 87 °C. TLC (pentane/Et₂O 2:1): R_f = 0.40 [UV, CAM]. IR (ATR): \tilde{v} (cm⁻¹) = 2956 (m, C-H), 1678 (s, C=O), 1629 (C=C), 1249 (s), 1179 (s), 807 (s). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.19 [s, 6H, C(CH₃)₂], 1.92 (s, 3H, CH₃), 2.47 (s, 2H, H-6), 2.49 (s, 2H, H-4), 6.99 (d, *J* = 2.5 Hz, 1H, H_{ar}), 7.22 (dd, *J* = 2.5 Hz, *J* = 9.0 Hz, 1H, H_{ar}), 7.30-7.35 (m, 1H, H_{ar}), 7.38-7.43 (m, 1H, H_{ar}), 7.63-7.65 (m, 1H, H_{ar}), 7.75-7.78 (m, 2H, H_{ar}). ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 18.3 (q, CH₃), 28.6 [q, C(CH₃)₂], 33.5 (s, C-5), 45.9 (t, C-4), 52.1 (t, C-6), 108.8 (d, C_{ar}), 117.8 (d, C_{ar}), 124.1 (d, C_{ar}), 126.5 (d, C_{ar}), 127.0 (d, C_{ar}), 127.8 (d, C_{ar}), 129.7 (d, C_{ar}), 129.9 (s, C_{ar}), 134.4 (s, C_{ar}), 143.9 (s, C_{ar}), 146.2 (s, C=C), 155.7 (s, C=C), 192.9 (s, C-1). MS (EI, 70 EV): *m*/*z* (%) = 280 (6) [M⁺], 237 (1) [(C₁₆H₁₃O₂)⁺], 205 (12), 144 (35) [(C₁₀H₇O)⁺], 115 (50), 82 (13). HRMS (EI, 70 eV): Calculated for C₁₉H₂₀O₂ [M⁺] = 280.1458. Found = 280.1453.

General procedure for racemic photoreactions. The irradiation precursor 1 (0.10 mmol) was transferred into a *Duran* tube and was dissolved in 10 mL deaerated dichloromethane. The mixture was irradiated at room temperature at $\lambda = 366$ nm until no starting material was detected by TLC. The solvent was removed under reduced pressure and the crude product was purified by column chromatography.

General procedure for enantioselective photoreactions at λ = 368 nm. Cu(ClO₄)₂·6H₂O (18.5 mg, 50.0 µmol, 0.50 equiv.) and bisoxazoline ligand 6c (21.8 mg, 60.0 µmol, 0.60 equiv.) were dissolved in 2 mL deaerated dichloromethane and stirred at room temperature for three hours. The irradiation precursor 1 (0.10 mmol, 1.00 equiv.) was dissolved in 5 mL deaerated dichloromethane and transferred by syringe into a Schlenk tube. The catalyst solution was transferred by syringe into the same Schlenk tube and the residual catalyst was washed with 2 × 1.5 mL of deaerated dichloromethane into the tube. The reaction mixture was irradiated at room temperature for the indicated period of time. The reaction mixture was diluted with 10 mL

dichloromethane and washed with 20 mL ethylenediaminetetraacetic acid (EDTA) solution. The aqueous phase was extracted with dichloromethane (3×15 mL), dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography to afford the corresponding photocyclisation product. If starting material was recovered the yield of recovered starting material (r.s.m.) is provided.

General procedure for sensitized enantioselective photoreactions at $\lambda = 419$ nm.

Cu(ClO₄)₂·6H₂O (18.5 mg, 50.0 μ mol, 0.5 equiv.) and the bisoxazoline ligand **6c** (21.8 mg, 6.00 μ mol, 0.6 equiv.) were dissolved in 2 mL deaerated dichloromethane and stirred at room temperature for three hours. The irradiation precursor **1** (0.10 mmol, 1.0 equiv.) and thioxanthone (10.6 mg, 50.0 μ mol, 0.5 equiv.) was dissolved in 5 mL deaerated dichloromethane and transferred by syringe into a *Duran* tube. The catalyst solution was transferred by syringe into the same *Duran* tube and the residual catalyst was washed with 2 × 1.5 mL of deaerated dichloromethane into the tube. The reaction mixture was irradiated at room temperature for 24 hours. The reaction mixture was diluted with 10 mL dichloromethane (3 × 15 mL), dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography to afford the corresponding photocyclisation product. If starting material was recovered the yield of recovered starting material (r.s.m.) is provided.

2,2,9b-Trimethyl-2,3,4a,9b-tetrahydro-1*H***-dibenzofuran-4-one** (*rac*-**3a**). According to the general procedure, compound **1a** (23.0 mg, 100 μmol) was irradiated (irradiation time: 22 h). Purification by column chromatography (pentane/Et₂O 8:1, CAM) gave the product as a colorless

oil (16.6 mg, 72 µmol, 72%). TLC: $R_f = 0.37$ (P/Et₂O 2:1) [CAM]. The spectroscopic data matched the literature values.^{2a}

The enantioselective reaction at $\lambda = 368$ nm was performed with 100 µmol **1a** (irradiation time 20 h) and gave product **3a** (12.2 mg) in 53% yield with 40% *ee*. $[\alpha]_D^{20} = -66.7$ (c = 0.51, CH₂Cl₂) [40% *ee*]. Chiral HPLC (OJ-RH, 150 × 4.6 mm, *MeCN* (A)/*H*₂*O* = 20% (A) \rightarrow 100% (A), 1 mL/min, $\lambda = 210$ nm, 254 nm): t_R [racemate] = 13.8 min (**3a**), 16.3 min (*ent*-**3a**). The enantioselective reaction at $\lambda = 419$ nm was performed with 100 µmol **1a** and gave product **3a** (13.2 mg) in 57% yield with 30% *ee*.

2,3,4a,9b-Tetrahydro-2,2,8,9b-tetramethyl-1*H***-dibenzofuran-4-one** (*rac***-3b**). According to the general procedure, compound **1b** (24.4 mg, 100 µmol) was irradiated (irradiation time: 24 h). Purification by column chromatography (pentane/Et₂O 8:1, CAM) gave the product as a colorless oil (13.2 mg, 54 µmol, 54%). TLC: $R_f = 0.33$ (P/Et₂O 2:1) [CAM]. The spectroscopic data matched the literature values.^{2a}

The enantioselective reaction at $\lambda = 368$ nm was performed with 100 µmol **1b** (irradiation time: 20 h) and gave product **3b** (11.0 mg) in 45% yield with 39% *ee*. [α]_D²⁰ = -35.4 (*c* = 0.57, CH₂Cl₂) [39% *ee*]. Chiral HPLC (OJ-RH, 150 × 4.6 mm, *MeCN* (A)/*H*₂*O* = 20% (A) \rightarrow 100% (A), 1 mL/min, $\lambda = 210$ nm, 254 nm): *t*_R [racemate] = 14.0 min (**3b**), 15.1 min (*ent*-**3b**). The enantioselective reaction at $\lambda = 419$ nm was performed with 100 µmol **1b** and gave product **3b** (7.5 mg) in 31% yield with 35% *ee*, 19% r.s.m.

8-tert-Butyl-2,2,9b-trimethyl-2,3,4a,9b-tetrahydro-1H-dibenzofuran-4-one (rac-3c).

According to the general procedure, compound **1c** (28.6 mg 100 μmol) was irradiated (irradiation time: 22 h). Purification by column chromatography (pentane/Et₂O 8:1, CAM) gave the product

as an orange oil (15.5 mg, 54 µmol, 54%). TLC: $R_f = 0.33$ (P/Et₂O 2:1) [CAM]. IR (ATR): \tilde{v} (cm⁻¹) = 2956 (m, C-H), 1727 (C=O), 1485 (s), 1026 (s), 817 (s). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.56 [s, 3H, C-2(CH₃)], 1.11 [s, 3H, C-2(CH₃)], 1.27 [s, 9H, C(CH₃)₃], 1.40 [s, 3H, C-9b(CH₃)], 1.94 (d, J = 14.6 Hz, 1H, CHH-1), 2.20 (dd, J = 12.8 Hz, J = 2.3 Hz, 1H, CHH-3), 2.26 (dd, J = 14.6 Hz, J = 2.3 Hz, 1H, CHH-1), 2.36 (d, J = 12.8 Hz, 1H, CHH-3), 4.50 (s, 1H, H-4a), 6.86 (d, J = 8.4 Hz, 1H, H_{ar}), 7.03 (d, J = 2.1 Hz, 1H, H_{ar}), 7.14 (dd, J = 8.4 Hz, J = 2.1 Hz, 1H, H_{ar}), 7.03 (d, J = 2.1 Hz, 1H, H_{ar}), 7.14 (dd, J = 8.4 Hz, J = 2.1 Hz, 1H, H_{ar}). ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 27.2 [q, C-2(CH₃)], 31.8 [q, C(CH₃)₃], 32.2 [q, C-9b(CH₃)], 32.5 [q, C-2(CH₃)], 34.5 [s, C(CH₃)₃], 36.1 [s, C-2], 46.1 (t, C-1), 49.6 (s, C-9b), 51.9 (t, C-3), 91.1 (d, C-4a), 109.8 (d, Car), 118.8 (d, Car), 125.1 (d, Car), 133.8 (s, Car), 144.6 (s, Car), 155.7 (s, Car), 208.7 (s, C-4). MS (EI, 70 eV): m/z (%) = 286 (23) [M⁺], 271 (100) [(C₁₈H₂₃O₂)⁺], 173 (24), 153 (53), 57 (48). HRMS (EI, 70 eV): Calculated for C₁₉H₂₆O₂ [M⁺] = 286.1927. Found = 286.1923.

The enantioselective reaction at $\lambda = 368$ nm was performed with 100 µmol **1c** (irradiation time: 24 h) and gave product **3c** (9.1 mg) in 32% yield with 39% *ee*, 17% r.s.m. $[\alpha]_D^{20} = -7.4$ (c = 0.55, CH₂Cl₂) [46% *ee*]. Chiral HPLC (AS-RH, 150 × 4.6 mm, *MeCN* (A)/*H*₂*O* = 20% (A) \rightarrow 100% (A), 1 mL/min, $\lambda = 210$ nm, 254 nm): t_R [racemate] = 16.9 min (*ent*-**3c**), 18.2 min (**3c**). The enantioselective reaction at $\lambda = 419$ nm was performed with 100 µmol **1c** and gave product **3c** (9.2 mg) in 32% yield with 46% *ee*, 32% r.s.m.

8-Methoxy-2,2,9b-trimethyl-2,3,4a,9b-tetrahydro-1*H*-dibenzofuran-4-one (*rac*-3d). According to the general procedure, compound 1d (26.0 mg, 100 µmol) was irradiated (irradiation time: 9 h). Purification by column chromatography (pentane/Et₂O 8:1, CAM) gave the product as a yellow solid (13.0 mg, 50 µmol, 50%). TLC: $R_f = 0.21$ (P/Et₂O 2:1) [CAM]. The spectroscopic data matched the literature values.^{2a}

The enantioselective reaction at $\lambda = 368$ nm was performed with 100 µmol **1d** (irradiation time: 24 h) and gave product **3d** (6.0 mg) in 26% yield with 34% *ee*, 17% r.s.m. $[\alpha]_D^{20} = -19.0$ (c = 0.53, CH₂Cl₂) [34% *ee*]. Chiral HPLC (AS-RH, 150 × 4.6 mm, *MeCN* (A)/*H*₂*O* = 20% (A) \rightarrow 100% (A), 1 mL/min, $\lambda = 210$ nm, 254 nm): t_R [racemate] = 12.7 min (*ent*-**3d**), 14.3 min (**3d**). The enantioselective reaction at $\lambda = 419$ nm was performed with 100 µmol **1d** and gave product **3d** (16.0 mg) in 62% yield with 29% *ee*.

8-Acetyl-2,2,9b-trimethyl-2,3,4a,9b-tetrahydro-1*H*-dibenzofuran-4-one (*rac*-3e). According to the general procedure, compound 1e (27.2 mg, 100 μ mol) was irradiated (irradiation time: 14 h). Purification by column chromatography (pentane/Et₂O 2:1, CAM) gave the product as a colorless oil (12.0 mg, 44 μ mol, 44%). TLC: $R_f = 0.34$ (P/Et₂O 1:2) [CAM]. The spectroscopic data matched the literature values.^{2a}

The enantioselective reaction at $\lambda = 368$ nm was performed with 100 µmol **1e** (irradiation time: 17 h) and gave product **3e** (20.7 mg) in 76% yield with 22% *ee*. [α]_D²⁰ = -20.7 (*c* = 0.87, CH₂Cl₂) [27% *ee*]. Chiral HPLC (AD-H, 250 × 4.6 mm, *n*-heptane/*i*-PrOH = 90:10, 1 mL/min, $\lambda = 210$ nm, 254 nm): *t*_R [racemate] = 11.9 min (*ent*-**3e**), 14.3 min (**3e**). The enantioselective reaction at $\lambda = 419$ nm was performed with 100 µmol **1e** and gave product **3e** (3.0 mg) in 11% yield with 27% *ee*, 23% r.s.m.

8-Carbomethoxy-2,2,9b-trimethyl-2,3,4a,9b-tetrahydro-1*H*-dibenzofuran-4-one (*rac*-3f). According to the general procedure, compound 1f (28.8 mg, 100 µmol) was irradiated (irradiation time: 12 h). Purification by column chromatography (pentane/Et₂O 2:1, CAM) gave the product as a colorless oil (10.7 mg, 37 µmol, 37%). TLC: $R_f = 0.31$ (P/Et₂O 1:2) [CAM]. The spectroscopic data matched the literature values.^{2a}

The enantioselective reaction at $\lambda = 368$ nm was performed with 100 µmol **1f** (irradiation time: 24 h) and gave product **3f** (14.6 mg) in 51% yield with 27% *ee*, 23% r.s.m. $[\alpha]_D^{20} = -31.0$ (c = 0.65, CH₂Cl₂) [27% *ee*]. Chiral HPLC (AD-H, 250 × 4.6 mm, *n*-heptane/*i*-PrOH = 90:10, 1 mL/min, $\lambda = 210$ nm, 254 nm): t_R [racemate] = 9.0 min (*ent*-**3f**), 10.2 min (**3f**). The enantioselective reaction at $\lambda = 419$ nm was performed with 100 µmol **1f** and gave product **3f** (5.0 mg) in 17% yield with 47% *ee*, 66% r.s.m.

8-Cyano-2,2,9b-trimethyl-2,3,4a,9b-tetrahydro-1H-dibenzofuran-4-one (rac-3g). According to the general procedure, compound 1g (25.5 mg, 100 µmol) was irradiated (irradiation time: 5 h). Purification by column chromatography (pentane/Et₂O 3:2, CAM) gave the product as a white solid (10.3 mg, 40 μ mol, 40%). m.p.: 121 °C. TLC: $R_f = 0.33$ (P/Et₂O 1:2) [CAM]. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.57 [s, 3H, C-2(CH₃)], 1.13 [s, 3H, C-2(CH₃)], 1.41 [s, 3H C-9b(CH₃)], 2.00 (d, J = 14.9 Hz, 1H, CHH-1), 2.22-2.26 (m, 2H, CHH-1, CHH-3), 2.40 (d, J = 13.1 Hz, 1H, CHH-3), 4.65 (s, 1H, H-4a), 7.02 (d, J = 8.2 Hz, 1H, H_{ar}), 7.31 (s, 1H, H_{ar}), 7.48 (d, J = 8.2 Hz, 1H, H_{ar}). ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 27.0 [q, C-2(CH₃)], 32.4 [q, C-2(*C*H₃)], 32.6 [q, C-9b(*C*H₃)], 36.1 (s, C-2), 45.9 (t, C-1), 49.1 (s, C-9b), 51.8 (t, C-3), 91.5 (d, C-4a), 105.1 (s, C_{ar}), 111.8 (d, C_{ar}), 119.3 (s, CN), 126.1 (d, C_{ar}), 134.0 (d, C_{ar}), 136.3 (s, C_{ar}), 161.4 (s, C_{ar}), 206.2 (s, C-4). MS (EI, 70 eV): m/z (%) = 255 (61) [M⁺], 240 (34) [($C_{15}H_{14}NO_{2}$)⁺], 198 (46), 156 (100), 83 (78). HRMS (EI, 70 eV): Calculated for $(C_{16}H_{17}NO_2)$ [M⁺] = 255.1254. Found = 255.1272. The enantioselective reaction at λ = 368 nm was performed with 100 µmol 1g (irradiation time: 23 h) and gave product **3g** (13.3 mg) in 52% yield with 30% *ee*. $[\alpha]_D^{20} = -25.9$ $(c = 0.54, CH_2Cl_2)$ [30% ee]. Chiral HPLC (AD-H, 250 × 4.6 mm, *n*-heptane/*i*-PrOH = 90:10, 1 mL/min, $\lambda = 210$ nm, 254 nm): $t_{\rm R}$ [racemate] = 13.7 min (*ent*-**3g**), 16.7 min (**3g**). The enantioselective reaction at $\lambda = 419$ nm was performed with 100 µmol **1g** and gave no product.

8-Bromo-2,2,9b-trimethyl-2,3,4a,9b-tetrahydro-1H-dibenzofuran-4-one (rac-3h). According to the general procedure, compound **1h** (30.9 mg, 100 µmol) was irradiated (irradiation time: 4 h). Purification by column chromatography (pentane/Et₂O 8:1, CAM) gave the product as a colorless solid (15.0 mg, 49 μ mol, 49%). m.p.: 86 °C. TLC: $R_f = 0.33$ (P/Et₂O 2:1) [CAM]. IR (ATR): \tilde{v} (cm⁻¹) = 2958 (m, C-H), 1722 (s, C=O), 1456 (s), 1180 (s), 1017 (s), 809 (s), 641 (s). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.60 [s, 3H, C-2(CH₃)], 1.12 [s, 3H, C-2(CH₃)], 1.40 (s, 3H, C-9b(CH₃)], 1.94 (d, J = 14.8 Hz, 1H, CHH-1), 2.20-2.24 (m, 2H, CHH-1, CHH-3), 2.37 (d, J = 12.7 Hz, 1H, CHH-3), 4.54 (s, 1H, H-4a), 6.83 (d, J = 8.5 Hz, 1H, H_{ar}), 7.13 (d, J = 2.1 Hz, 1H, H_{ar}), 7.24 (dd, J = 8.5 Hz, J = 2.1 Hz, 1H, H_{ar}), ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) $= 27.1 [q, C-2(CH_3)], 32.4 [q, C-2(CH_3)], 32.4 [q, C-9b(CH_3)], 36.1 (s, C-2), 46.0 (t, C-1), 49.6$ (s, C-9b), 51.8 (t, C-3), 91.1 (d, C-4a), 112.4 (d, C_{ar}), 113.5 (s, C_{ar}), 125.1 (d, C_{ar}), 131.4 (d, C_{ar}), 136.9 (s, C_{ar}), 157.0 (s, C_{ar}), 207.2 (s, C-4). MS (EI, 70 eV): m/z (%) = 308 (61) [M⁺], 293 (31) $[(C_{14}H_{14}BrO_2)^+]$, 251 (22), 210 (96), 83 (100). HRMS (EI, 70 eV): Calculated for $(C_{15}H_{17}^{-79}BrO_2)$ $[M^+] = 308.0406$. Found = 308.0404. Calculated for $(C_{15}H_{17}^{81}BrO_2) [M^+] = 310.0386$. Found = 310.0383. The enantioselective reaction at $\lambda = 368$ nm was performed with 100 µmol **1h** (irradiation time: 23 h) and gave product **3h** (20.1 mg) in 65% yield with 26% *ee*. $[\alpha]_D^{20} = -15.7$ (c = 0.51, CH₂Cl₂) [30% ee]. Chiral HPLC (AD-H, 250 × 4.6 mm, n-heptane/i-PrOH = 90:10, 1 mL/min, $\lambda = 210$ nm, 254 nm): $t_{\rm R}$ [racemate] = 10.3 min (*ent*-**3h**), 13.2 min (**3h**). The enantioselective reaction at $\lambda = 419$ nm was performed with 100 µmol **1h** and gave product **3h** (12.0 mg) in 39% yield with 30% ee.

10,10,11a-Trimethyl-9,10,11,11a-tetrahydronaphtho[**2,1-b**]**benzofuran-8(7aH)-one** (*rac*-**3i**). According to the general procedure, compound **1i** (28.0 mg, 100 μmol) was irradiated (irradiation

time: 15 h). Purification by column chromatography (pentane/Et₂O 8:1, CAM) gave the product as an orange solid (16.0 mg, 57 μ mol, 57%). m.p.: 119-121 °C. TLC: $R_f = 0.41$ (P/Et₂O 2:1) [CAM]. IR (ATR): \tilde{v} (cm⁻¹) = 2924 (m, C-H), 1715 (s, C=O), 1263 (m), 1028 (s), 804 (s), 744 (m). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.64 [s, 3 H, C-10(CH₃)], 1.17 [s, 3H, C-10(CH₃)], 1.67 [s, 3H, C-11a(CH₃)], 2.15 (d, J = 14.8 Hz, 1H, CHH-9), 2.31 (dd, J = 13.6 Hz, J = 1.8 Hz 1H, CHH-11), 2.39 (d, J = 13.6 Hz, 1H, CHH-11), 2.78 (dd, J = 14.8 Hz, J = 1.8 Hz, 1H, CHH-9), 4.59 (s, 1H, H-7a), 7.23 (d, J = 8.8 Hz, 1H, H_{ar}), 7.31 (ddd, J = 8.1, J = 6.9, J = 1.1 Hz, 1H, H_{ar} , 7.47 (ddd, J = 8.4, J = 6.9, J = 1.4 Hz, 1H, H_{ar}), 7.69 (d, J = 8.8 Hz, 1H, H_{ar}), 7.80-7.82 (m, 1H, H_{ar}), 7.92-7.95 (m, 1H, H_{ar}). ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 27.0 [q, C-10(CH₃)], 30.4 [q, C-11a(CH₃)], 32.1 [q, C-10(CH₃)], 35.6 (s, C-10), 46.6 (t, C-11), 51.3 (s, C-11a), 51.5 (t, C-9), 91.2 (d, C-7a), 113.0 (d, Car), 121.6 (d, Car), 123.1 (d, Car), 124.6 (s, Car), 126.8 (d, C_{ar}), 129.8 (d, C_{ar}), 130.1 (s, C_{ar}), 130.3 (d, C_{ar}), 130.6 (s, C_{ar}), 156.0 (s, C_{ar}), 208.2 (s, C-8). MS (EI, 70 eV): m/z (%) = 280 (39) [M⁺], 265 (36) [(C₁₈H₁₇O₂)⁺], 237 (3) [(C₁₆H₁₃O₂)⁺], 220 (25), 205 (100), 182 (60), 153 (25), 83 (25). HRMS (EI, 70 eV): Calculated for (C₁₉H₂₀O₂) $[M^+] = 280.1458$. Found = 280.1456. The enantioselective reaction at $\lambda = 368$ nm was performed with 100 µmol 1i (irradiation time: 24 h) and gave product 3i (10.0 mg) in 36% yield with 28% *ee.* $[\alpha]_D^{20} = -43.1$ (*c* = 0.51, CH₂Cl₂) [9% *ee*]. Chiral HPLC (OJ-RH, 150 × 4.6 mm, MeCN) (A)/ $H_2O = 20\%$ (A) $\rightarrow 100\%$ (A), 1 mL/min, $\lambda = 210$ nm, 254 nm): t_R [racemate] = 16.0 min (3i), 16.5 min (*ent*-3i). The enantioselective reaction at $\lambda = 419$ nm was performed with 100 μ mol 1i and gave product 3i (16.0 mg) in 57% yield with 9% ee.

trans-2,2,9b-Trimethyl-2,3,4a,9b-tetrahydro-1*H*-dibenzofuran-4-one (*rac*-5a). According to the general procedure, compound 1a (23.0 mg, 100 μ mol) was irradiated (irradiation time: 22 h) in dry CH₂Cl₂. Purification by column chromatography (pentane/Et₂O 8:1, CAM) gave *cis*-

product *rac*-**3a** as a colorless oil (2.3 mg, 10 µmol, 10%) and *trans*-product *rac*-**5a** as a colorless oil (10.1 mg, 44µmol, 44%). TLC: $R_f = 0.61$ (P/Et₂O 2:1) [CAM]. IR (ATR): \tilde{v} (cm⁻¹) = 2928 (m, C-H), 1738 (s, C=O), 1459 (s), 1203 (s), 1044 (s), 748 (s). ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 1.14 (s, 3H, C-9b(CH₃), 1.27 [s, 3H, C-2(CH₃)], 1.28 [s, 3H, C-2(CH₃)], 2.21-2.27 (m, 2H, H-3), 2.46 (dd, *J* = 18.1 Hz, *J* = 1.0 Hz, 1H, CHH-1), 2.55 (d, *J* = 18.1 Hz, 1H, CHH-1), 4.94 (s, 1H, H-4a), 6.94-6.97 (m, 2H, H_{ar}), 7.08-7.10 (m, 1H, H_{ar}), 7.14-7.18 (m, 2H, H_{ar}). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ (ppm) = 23.0 (q, CH₃), 34.6 [q, C-2(CH₃)], 34.7 (s, C-2), 36.3 [q, C-2(CH₃)], 46.1 (t, C-3), 48.4 (s, C-9b), 53.0 (t, C-1), 92.1 (d, C-4a), 111.8 (d, C_{ar}), 121.7 (d, C_{ar}), 122.3 (d, C_{ar}), 128.5 (d, C_{ar}), 138.0 (s, C_{ar}), 158.4 (s, C_{ar}), 203.4 (s, C-4). MS (EI, 70 eV): m/z (%) = 230 (43) [M⁺], 215 (66) [(C₁₄H₁₅O₂)⁺], 173 (42) [(C₁₁H₁₉O₂)⁺], 145 (40), 131 (99), 83 (100). HRMS (EI, 70 eV): Calculated for (C₁₅H₁₈O₂) [M⁺] = 230.1301. Found: 230.1296.

2,2'-(Propane-2,2-diyl)bis[4-(4-(benzyloxy)benzyl)-4,5-dihydrooxazole] (**6d**). To a solution of 2,2-dimethylmalononitrile (128 mg, 1.36 mmol, 1.00 equiv.) in dry toluene was added Zn(OTf)₂ (989 mg, 2.72 mmol, 2.00 equiv.). The solution was stirred for 5 min at room temperature and (*S*)-2-amino-3-(4-benzyloxyphenyl)-1-propanol³¹ (700 mg, 2.72 mmol, 2.00 equiv.) was added. The solution was heated under reflux for 72 h. After cooling to room temperature, the solution was washed with saturated NaHCO₃-solution and brine, dried over Na₂SO₄ and filtered. After evaporation of the solvent, the crude material was purified by column chromatography (EtOAc). The product was obtained as a white solid (366 mg, 0.64 mmol, 47%). m.p.: 67 °C. TLC: $R_{\rm f} = 0.18$ (EtOAc) [KMnO₄]. IR (ATR): \tilde{v} (cm⁻¹) = 2894 (w, C-H), 1650 (s, C=N), 1510 (s), 1240 (s), 730 (s). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.45 [s, 6H, (CH₃)₂], 2.61 (dd, *J* = 13.8 Hz, *J* = 8.4 Hz, 2H, 2 × CHHPh), 3.01 (dd, *J* = 13.8 Hz, *J* = 4.7 Hz, 2H, 2 × CCHHPh), 3.99 (dd, *J* = 8.4 Hz, J = 6.9 Hz, 2H, 2 × OCHH), 4.16 (dd, *J* = 9.2 Hz, J = 8.4 Hz, 2H, 2 × OCHH), 4.32-

4.40 (m, 2H, 2 × CH), 5.03 (s, 4H, 2 × OCH₂Ph), 6.88-6.91 (m, 4H, H_{ar}), 7.09-7.13 (m, 4H, H_{ar}), 7.29-7.34 (m, 2H, H_{ar}), 7.36-7.43 (m, 8H, H_{ar}). ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 24.4 (q, [C(CH₃)], 38.7 [s, C(CH₃)₂], 40.5 (t, CH₂Ph), 67.3 (d, CH), 70.2 (t, OCH₂Ph), 72.1 (t, OCH₂), 115.0 (d, C_{ar}), 127.6 (d, C_{ar}), 128.1 (d, C_{ar}), 128.7 (d, C_{ar}), 130.2 (s, C_{ar}), 130.6 (d, C_{ar}), 137.3 (s, C_{ar}), 157.7 (s, C_{ar}), 165.5 (s, NCO). HRMS (ESI): Calculated for C₃₇H₃₉N₂O₄ [(M+H)⁺] = 575.2865. Found = 575.2908.

3-Methyl-2-phenoxy-2-cyclohexen-1-one (7a, R = Me). To a solution of phenol (709 mg, 7.53 mmol, 0.95 equiv.) in dry THF (20 mL) was added KH in mineral oil (30%, 106 mg, 0.79 mmol, 0.1 equiv.) and stirred at room temperature for 10 min. After addition of 2,3-epoxy-3methylcyclohexanone³² (1.00 g, 7.93 mmol, 1.00 equiv.), DMPU (786 µL, 6.50 mmol, 0.82 equiv.) was added. The reaction mixture was stirred at reflux for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and water. After separation of the layers, the aqueous phase was extracted three times with CH₂Cl₂ (15 mL). The combined organic phases were washed with brine (60 mL), dried over Na₂SO₄ and filtered. After evaporation the crude material was purified by column chromatography (pentane/Et₂O 5:1, CAM). The product (537 mg, 2.66 mmol, 33%) could be isolated as a yellow oil, which crystallized upon standing. m.p.: 39 °C. TLC (pentane/Et₂O 2:1): $R_{\rm f} = 0.29$ [UV, CAM]. IR (ATR): \tilde{v} (cm⁻¹) = 2953 (w, C-H), 2923 (w, C-H), 1667 (s, C=O), 1640 (s, C=C), 1589 (s), 1491 (s), 1220 (s), 1128 (s), 754 (s, C-H), 741 (s, C-H), 650 (s, C-H). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.93 (s, 3H, CH₃), 2.07-2.13 (m, 2H, CH₂), 2.55-2.58 (m, 4H, $2 \times CH_2$), 6.85-6.87 (m, 2H, H_{ar}), 6.97-7.00 (m, 1H, H_{ar}), 7.25-7.29 (m, 2H, H_{ar}). ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 18.1 (q, CH₃), 22.2 (t, CH₂), 31.8 (t, CH₂), 38.5 (t, CH₂), 114.8 (d, C_{ar}), 121.8 (d, C_{ar}), 129.6 (d, C_{ar}), 144.3 (s, C_{ar}), 148.8 (s, C-2), 157.7 (s, C-3), 193.1 (s,

C-1). MS (EI, 70 EV): m/z (%) = 202 (100) [M⁺], 187 (11) [(M-CH₃)⁺], 174 (21) [(C₁₁H₁₀O₂)⁺], 159 (13) [(C₁₀H₇O₂)⁺], 145 (20) [(C₉H₅O₂)⁺], 77 (15) [(C₆H₅)⁺]. HRMS (EI, 70 eV): Calculated for C₁₃H₁₄O₂ [M⁺] = 202.0988. Found = 202.0983.

3-(4-Pentenyl)-2-phenoxy-2-cyclohexen-1-o ne (**7b**, R = 4-pentenyl). To a solution of phenol (326 mg, 3.47 mmol, 1.00 equiv.) in dry DMSO (10 mL) was added KH in mineral oil (30%, 46 mg, 0.35 mmol, 0.10 equiv.) and stirred at room temperature for 10 min. After addition of 6-(4-pentenyl)-7-oxabicyclo[4.1.0]heptan-2-one^{4c} (664 mg, 3.64 mmol, 1.05 equiv.), DMPU (344 μ L, 2.85 mmol, 0.82 equiv.) was added. The reaction mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the solution was extracted with Et₂O (3 × 10 mL). The combined organic layers were washed with brine (35 mL), dried over Na₂SO₄ and filtered. After evaporation the crude material was purified by column chromatography (pentane/Et₂O 10:1, UV, CAM) gave the product as a yellow oil (618 mg, 2.41 mmol, 69%). TLC: *R*_f = 0.48 (P/Et₂O 1:1) [UV, CAM]. The spectroscopic data matched the literature values.^{4c}

9b-Methyl-2,3,4a,9b-tetrahydro-1H-dibenzofuran-4-one (*rac-8*). According to the general procedure, compound **7a** (20.2 mg, 100 μmol) was irradiated (irradiation time: 24 h). Purification by column chromatography (pentane/Et₂O 8:1, CAM) gave the product as a yellow solid (12.0 mg, 59 μmol, 59%). m.p.: 71 °C. TLC: $R_f = 0.41$ (P/Et₂O 2:1) [CAM]. IR (ATR): \tilde{v} (cm⁻¹) = 2965 (w, C-H), 2929 (w, C-H), 1719 (m, C=O), 1472 (m), 1459 (m), 1027 (m), 740 (s), 752 (s). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.44 (s, 3H, CH₃), 1.63-1.73 (m, 1H, CHH-2), 1.83 (t, *J* = 13.3 Hz, 1H, CHH-1), 1.86-1.96 (m, 1H, CHH-2), 2.03-2.06 (m, 1H, CHH-1), 2.32-2.40 (m, 1H, CHH-3), 2.54-2.58 (m, 1H, CHH-3), 4.46 (s, 1H, H-9b), 6.91-6.95 (m, 2H, H_{ar}) 7.05 (d, *J* = 7.2 Hz, 1H, H_{ar}), 7.17 (t, *J* = 7.6 Hz, 1H, H_{ar}). ¹³C {¹H} NMR (101 MHz, CDCl₃): δ (ppm) =

20.8 (t, C-2), 28.2 (q, CH₃), 34.6 (t, C-1), 38.4 (t, C-3), 50.2 (s, C-9b), 91.8 (d, C-4a), 110.5 (d, C_{ar}), 121.8 (d, C_{ar}), 122.1 (d, C_{ar}), 128.8 (d, C_{ar}), 133.6 (s, C_{ar}), 159.1 (s, C_{ar}), 208.6 (s, C-4). MS (EI, 70 eV): m/z (%) = 202 (87) [M⁺], 187 (38) [(C₁₂H₁₁O₂)], 159 (24) [(C₁₀H₇O₂)⁺], 145 (95) [(C₉H₅O₂)⁺], 131 (100), 77 (18) [(C₆H₅)⁺]. HRMS (EI, 70 eV): Calculated for (C₁₃H₁₄O₂) [M⁺] = 202.0988. Found: 202.0985.

The enantioselective reaction at $\lambda = 368$ nm was performed with 100 µmol **7a** (irradiation time: 24h) and gave product **8** (13.9 mg) in 69% yield with 20% *ee*. [α]_D²⁰ = -9.9 (*c* = 0.41, CH₂Cl₂) [20% *ee*]. Chiral HPLC (AS-RH, 150 × 4.6 mm, *MeCN* (A)/*H*₂*O* = 20% (A) \rightarrow 100% (A), 1 mL/min, $\lambda = 210$ nm, 254 nm): *t*_R [racemate] = 11.9 min (*ent*-**8**), 12.6 min (**8**).

6-Phenoxy-[6.3.0.0^{1,6}]undecan-5-one (*rac-9*). According to the general procedure, compound 7b (25.6 mg, 100 µmol) was irradiated (irradiation time: 10 h). Purification by column chromatography (pentane/Et₂O 10:1, CAM) gave the product as a yellow oil (20.0 mg, 78 µmol, 78%). TLC: $R_{\rm f} = 0.66$ (P/Et₂O 2:1) [UV, CAM]. The spectroscopic data matched the literature values.^{4c}

An enantioselective reaction at $\lambda = 368$ nm was attempted with 100 µmol **7b** (irradiation time: 19 h) but product *rac*-**9** (63% yield) showed no *ee*. Chiral HPLC (OJ-RH, 150 × 4.6 mm, *MeCN* (A)/*H*₂*O* = 20% (A) \rightarrow 100% (A), 1 mL/min, $\lambda = 210$ nm, 254 nm): *t*_R [racemate] = 19.6 min, 20.4 min.

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SUPPLEMENTARY MATERIAL

Additional UV/Vis data for Lewis acid coordination, the O_2 quenching study, ¹H- and ¹³C-NMR spectra of all compounds reported in the Experimental Section, HPLC traces of enantioenriched products **3**, X-ray data for the crystal structure of compound **3h**, emission spectra of the LED.

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¹⁷ For the emission spectrum of the LED, see the Supplementary Data.

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