Enantioselective photocyclisation reactions of 2-aryloxycyclohex-2-enones mediated by a chiral copper-bisoxazoline complex

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A B S T R A C T

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-1H-dibenzofuran-4-ones (nine examples, 37–74% yield). Since it was found that the substrates show a significant bathochromic absorption shift upon treatment with EtAlCl$_2$, it was attempted to perform the reactions enantioselectively in the presence of a chiral Lewis acid. A complex of Cu(ClO$_4$)$_2$·6H$_2$O 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.

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1. 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 h 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 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]

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 [6π]-photocyclisation[6,7] of 2-aryloxycyclohex-2-enones[8] in the context of our work[9] on Lewis-acid catalyzed enantioselective photochemical reactions.[10] It was found that Lewis acid coordination[11] to cyclic alkenones leads to a bathochromic shift of the intense ($\varepsilon \cong 15000$ M^{-1} cm^{-1}) ππ* absorption. Due to this shift, the strong absorption of the Lewis acid complex overlaps the weak ($\varepsilon \leq 100$ M^{-1} cm^{-1}) nπ* 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 (Fig. 1) suggested that the plan could be viable as compound **1a** exhibited a

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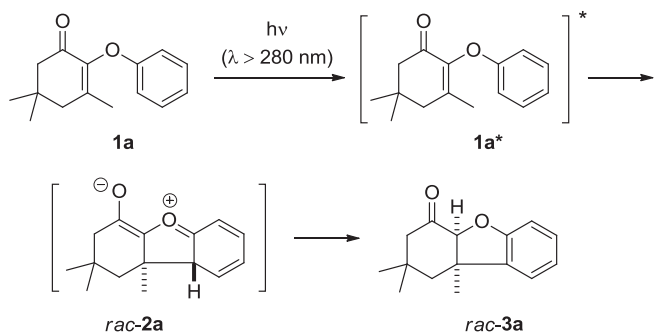
Scheme 1. Proposed reaction pathway for the photocyclisation of 2-phenyloxycyclohex-2-enone **1a** to product *rac*-**3a**.
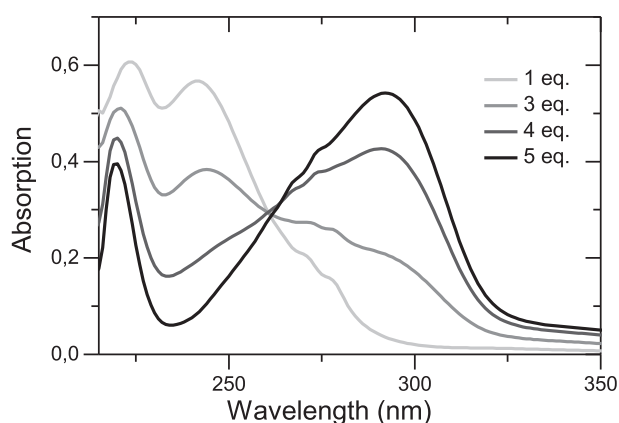

Fig. 1. UV–Vis spectra of compound **1a** in the presence of various amounts of EtAlCl$_2$.

significant bathochromic shift upon addition of EtAlCl$_2$ as the Lewis acid.

The strong absorption with maxima at $\lambda = 223$ nm ($\varepsilon = 11450$ M^{-1} cm^{-1}) and at $\lambda = 241$ nm ($\varepsilon = 10460$ M^{-1} cm^{-1}) vanished upon Lewis acid addition and a new band appeared with a maximum at $\lambda = 292$ nm ($\varepsilon = 10840$ M^{-1} cm^{-1}). The strong band stretches into a wavelength region, in which the weak nπ^* absorption of the uncomplexed enone **1a** occurs ($\lambda = 320$ nm, $\varepsilon = 114$ M^{-1} 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.

2. Results

2.1. 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.

Table 1
Formation of substrates **1** by epoxide ring opening/elimination from isophorone oxide (*rac*-**4**) and subsequent photocyclisation to racemic products *rac*-**3**.
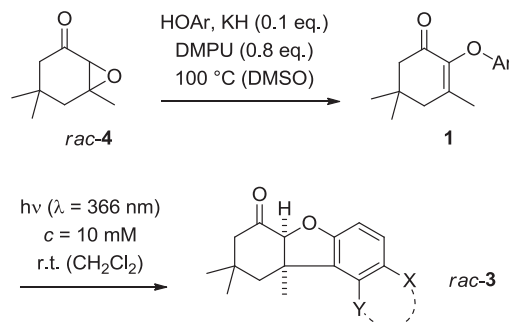
Entry	Ar	1	yield[a] [%]	*rac*-3	*t* [h][b]	yield[c] [%]
1		**1a**	72	*rac*-**3a**	24	72
2		**1b**	77	*rac*-**3b**	24	54
3		**1c**	83	*rac*-**3c**	22	54
4		**1d**	39[d]	*rac*-**3d**	9	50
5		**1e**	80	*rac*-**3e**	14	44
6		**1f**	37	*rac*-**3f**	12	37
7		**1g**	61	*rac*-**3g**	5	40
8		**1h**	87	*rac*-**3h**	4	49[e]
9		**1i**	80	*rac*-**3i**	15	57

[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.

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 **1a** → *rac*-**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]

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 established[5] and was confirmed.

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 λ = 368 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. K_2CO_3 in wet CH_2Cl_2), compound *rac*-**5a** was quantitatively transformed into *cis*-diastereoisomer *rac*-**3a**.

2.2. 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.

The ligand screen was performed with $Cu(OTf)_2$[18] and chiral oxazoline ligands[19] in deaerated dichloromethane solution and a few selected results are summarized in Table 2. As expected from previous work[9] 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 CH_2Cl_2 solution (c = 10 mM, λ = 366 nm, t = 24 h). Among the various metal salts, there was only a single beneficial effect to be observed when $Cu(ClO_4)_2 \cdot 6H_2O$ 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

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

Entry[a]	Ligand	yield[b] [%]	e.r.[c]	ee[d] [%]
1	**6a** (^{t}Bu)	44	55/45	10
2	**6b** (Ph)	52	43/57	14
3	**6c** (Bn)	47	60/40	20
4	**6d** (PBB)	52	56/44	12
5	**6e** (Bn)	20[e]	50/50	−
6	**6f** (Bn)	35[f]	50/50	−
7	**6g** (^{t}Bu)	44	50/50	−

[a] The reaction was run to completion (20−24 h reaction time) unless indicated otherwise.
[b] Yield of isolated product.
[c] The 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 24 h.
[f] 65% conversion after 24 h.

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 $Cu(ClO_4)_2 \cdot 6H_2O$ was increased from 0.5 to 1.0 equivalents, the yield increased but the enantioselectivity decreased (53%, 36% *ee*). If the ligand loading was increased to 1.0 equiv. and the loading of $Cu(ClO_4)_2 \cdot 6H_2O$ was kept at 0.5 equiv. there was a significant increase in enantioselectivity but the yield did not improve (34%, 60% *ee*).

c (H_2O) < 20 ppm	10%	44%
c (H_2O) > 50 ppm	61%	—
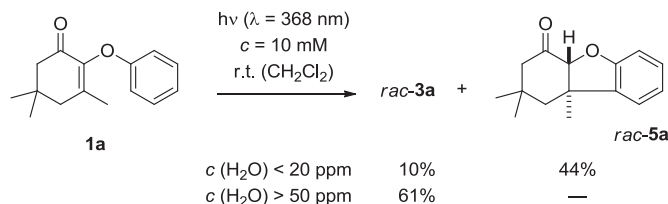
Scheme 2. Influence of the water content of the solvent on the relative configuration of photocyclisation products from substrate **1a**.

2.3. 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 flask[21] 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 re- actions 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 and 76%. The enantio- selectivity 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.
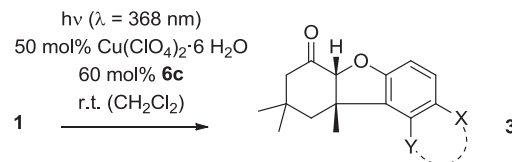
The absolute configuration of the major enantiomer in the re- action **1h → 3h** could be elucidated by anomalous X-ray diffraction (Fig. 2). In order to obtain a configurationally homogenous sample the *ee* of the compound was enriched by chiral semipreparative HPLC to >99%. The identity of the enantiomer, of which the crystal structure was determined, was confirmed by subsequent HPLC analysis.

As in the solid-state reaction of 2-arylthiocyclohex-2-enones,[8] the enantioface differentiation in the current photocyclisation re- action 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 Fig. 3.

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 $Cu(H_2O)_2(SbF_6)_2 \cdot$**6a** for example revealed that there is a positive dihedral angle between the marked atoms $O^1-Cu-N^1-C^1$ of ca. $+30°$.[21a] A similar dihedral angle is observed for $O^2-Cu-N^2-C^2$ 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 $Cu(H_2O)_2(SbF_6)_2 \cdot$**6b** the above-mentioned dihedral angles are negative[20,21b] inducing a twist of substrate **1a** in the opposite di- rection with the *Si* face now being more readily accessible. Another aspect deserves to be mentioned. If one assumes an initial coordi- nation as shown in Fig. 3, the ether oxygen atom of the substrate

Table 3
Cu-Mediated enantioselective photocyclisation of 2-aryloxy–cyclohex-2-enones **1** to products **3** upon direct irradiation at λ = 368 nm.

Entry[a]	Product	t [h][b]	r.s.m.[c] [%]	yield[d] [%]	ee[e] [%]
1	**3a**	20	–	53	40
2	**3b**	20	–	45	39
3	**3c**	24	17	32	39
4	**3d**	24	17	26	39
5	**3e**	17	–	76	22
6	**3f**	24	23	51	27
7	**3g**	23	–	52	30
8	**3h**	23	–	65	26
9	**3i**	24	–	36	28

[a] All reactions were performed on a scale of 0.1 mmol (*c* = 10 mM) with a LED lamp (3 W power output)[16] 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.

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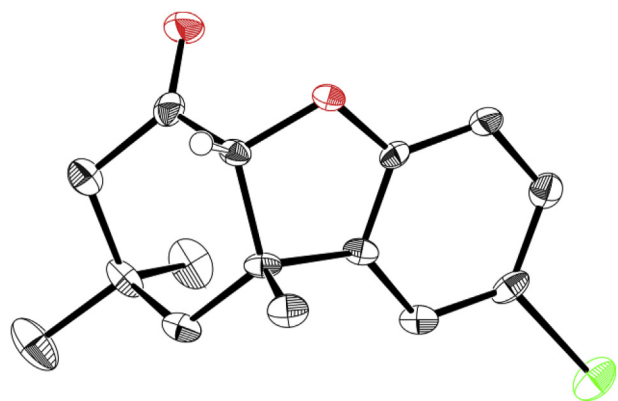
Fig. 2. Absolute configuration of product **3h** as determined by anomalous X-ray diffraction.

chelation may be a reason for the only moderate enantioselectivity of the photocyclisation.

2.4. 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 process[23] 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
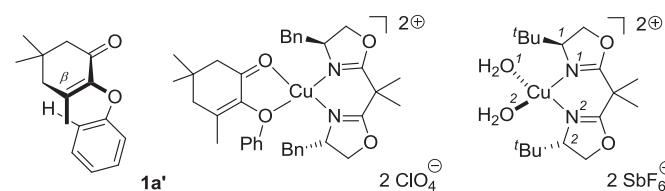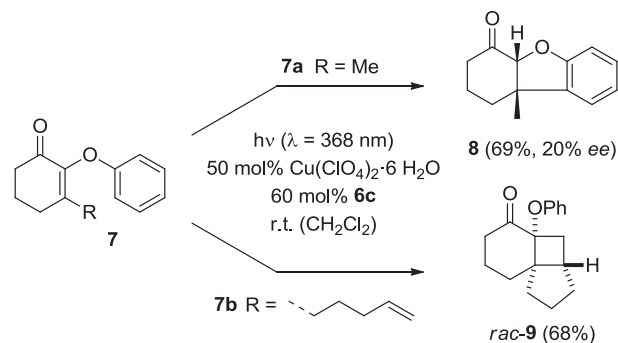

Fig. 3. Twisted conformation **1a'** of substrate **1a**, possible coordination of **1a** to the Cu bisoxazoline complex Cu(ClO$_4$)$_2$·**6c**, and structure of Cu(H$_2$O)$_2$(SbF$_6$)$_2$·**6a**.

Scheme 3. Photocyclisation vs. [2+2] photocycloaddition in the reaction of substrates **7**.

Table 4
Cu-Mediated enantioselective photocyclisation of 2-aryloxy¬cyclohex-2-enones **1** to products **3** upon sensitized excitation at $\lambda = 419$ nm.
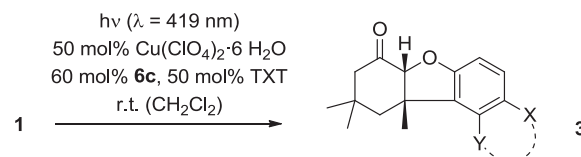
Entry[a]	Product	r.s.m.[b] [%]	yield[c] [%]	ee[d] [%]
1	**3a**	–	57	30
2	**3b**	19	31	35
3	**3c**	32	32	46
4	**3d**	–	62	29
5	**3e**	23	11	27
6	**3f**	66	17	47
7	**3g**	75	–[e]	–
8	**3h**	–	39	30
9	**3i**	–	57	9

[a] All reactions were performed on a scale of 0.1 mmol ($c = 10$ mM) with a set of fluorescence lamps (RPR-4190 Å)[15c] as the light source. The reaction time was in all cases 24 h.
[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.

the addition of 50 mol% of the sensitizer enabled a conversion of several substrates upon irradiation at $\lambda = 419$ nm for 24 h (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 sensitizer[24] 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).

3. Conclusion

In summary, we have discovered the first enantioselective photocyclisation reactions of 2-aryloxycyclohex-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$_4$)$_2$·6H$_2$O 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 ($\varepsilon = 114$ M^{-1} cm^{-1}). The long-wavelength 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]

4. Experimental section

4.1. 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 (CH_2Cl_2) 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 (Et$_2$O), dichloromethane (CH_2Cl_2), methanol (MeOH)] were distilled prior to use. The following compounds were prepared according to published procedures: *rac*-**4**,[14] **6a**,[21a] **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 ($\lambda = 368$ nm)[16] 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.[20] 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 min. 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), KMnO$_4$ 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 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). ^{1}H and ^{13}C 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 (^{1}H) = 7.26 ppm, δ (^{13}C) = 77.16 ppm]. All coupling constants (J) are reported in Hertz (Hz). The relative configuration of chiral products and the multiplicity of the ^{13}C 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.

4.1.1. 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 oxide[14] (*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 Et$_2$O (5 mL/mmol). The combined organic layers were washed with brine (10 mL/mmol), dried over Na$_2$SO$_4$ and filtered. After evaporation the crude material was purified by column chromatography.

4.1.1.1. 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/Et$_2$O 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/Et$_2$O 2:1) [UV, CAM]. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2954 (m, C—H), 1676 (C=O), 1508 (s), 1230 (s), 1181 (s), 835 (s), 827 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.14 [s, 6H, C(CH$_3$)$_2$], 1.28 [s, 9H, C(CH$_3$)$_3$], 1.89 (s, 3H, CH$_3$), 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$_{ar}$). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 18.3 (q, CH$_3$), 28.6 [q, C(CH$_3$)$_2$], 31.7 [q, C(CH$_3$)$_3$], 33.4 (s, C-5), 34.2 [s, *C*(CH$_3$)$_3$], 45.8 (t, C-4), 52.1 (t, C-6), 114.3 (d, C$_{ar}$), 126.5 (d, C$_{ar}$), 143.9 (s, C^{t}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 C$_{19}$H$_{26}$O$_2$ [M$^+$] = 286.1927. Found = 286.1925.

4.1.1.2. 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/Et$_2$O 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/Et$_2$O 1:2) [UV, CAM]. IR (ATR): $\tilde{\nu}$ (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). ^{1}H NMR (360 MHz, CDCl$_3$): δ (ppm) = 1.15 [s, 6H, C(CH$_3$)$_2$], 1.89 (s, 3H, CH$_3$), 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$_{ar}$). ^{13}C {^{1}H} NMR (90 MHz, CDCl$_3$): 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): 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 C$_{16}$H$_{17}$NO$_2$ [M$^+$] = 255.1258. Found = 255.1254.

4.1.1.3. 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/Et$_2$O 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/Et$_2$O 2:1) [UV, CAM]. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957 (m, C–H), 1668 (s, C=C), 1479 (s), 1227 (s), 823 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.14 [s, 6H, C(CH$_3$)$_2$], 1.88 (s, 3H, CH$_3$), 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$_{ar}$). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 18.2 (q, CH$_3$), 28.6 [q, C(CH$_3$)$_2$], 33.4 (s, C-5), 45.8 (t, C-4), 51.9 (t, C-6), 114.1 (s, C$_{ar}$), 116.8 (d, C$_{ar}$), 132.5 (d, C$_{ar}$), 143.6 (s, C=C), 146.3 (s, C=C), 156.9 (s, C$_{ar}$), 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 C$_{15}$H$_{17}$O$_2^{79}$Br [M$^+$] = 308.0414. Found = 308.0406. Calculated for C$_{15}$H$_{17}$O$_2^{81}$Br [M$^+$] = 310.0386. Found = 310.0393.

4.1.1.4. 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/Et$_2$O 10:1, UV, CAM) gave the product as a light yellow solid (695 mg, 2.48 mmol, 80%). m.p.: 87 °C. TLC (pentane/Et$_2$O 2:1): R_f = 0.40 [UV, CAM]. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2956 (m, C–H), 1678 (s, C=O), 1629 (C=C), 1249 (s), 1179 (s), 807 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.19 [s, 6H, C(CH$_3$)$_2$], 1.92 (s, 3H, CH$_3$), 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$_{ar}$). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 18.3 (q, CH$_3$), 28.6 [q, C(CH$_3$)$_2$], 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) [(C$_{16}$H$_{13}$O$_2$)$^+$], 205 (12), 144 (35) [(C$_{10}$H$_7$O)$^+$], 115 (50), 82 (13). HRMS (EI, 70 eV): Calculated for C$_{19}$H$_{20}$O$_2$ [M$^+$] = 280.1458. Found = 280.1453.

4.1.2. Photocyclisation reactions

4.1.2.1. 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 λ = 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.

4.1.2.2. General procedure for enantioselective photoreactions at λ = 368 nm. Cu(ClO$_4$)$_2$·6H$_2$O (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 Na$_2$SO$_4$, 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.

4.1.2.3. General procedure for sensitized enantioselective photoreactions at λ = 419 nm. Cu(ClO$_4$)$_2$·6H$_2$O (18.5 mg, 50.0 µmol, 0.5 equiv.) and the bisoxazoline ligand **6c** (21.8 mg, 60.0 µmol, 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 µmol, 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 h. The reaction mixture was diluted with 10 mL dichloromethane and washed with 20 mL EDTA solution. The aqueous phase was extracted with dichloromethane (3 × 15 mL), dried over Na$_2$SO$_4$, 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.

4.1.2.4. 2,2,9b-Trimethyl-2,3,4a,9b-tetrahydro-1H-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/Et$_2$O 8:1, CAM) gave the product as a colorless oil (16.6 mg, 72 µmol, 72%). TLC: R_f = 0.37 (P/Et$_2$O 2:1) [CAM]. The spectroscopic data matched the literature values.[2a]

The enantioselective reaction at λ = 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, CH$_2$Cl$_2$) [40% *ee*]. Chiral HPLC (OJ-RH, 150 × 4.6 mm, *MeCN* (A)/*H$_2$O* = 20% (A) → 100% (A), 1 mL/min, λ = 210 nm, 254 nm): t_R [racemate] = 13.8 min (**3a**), 16.3 min (*ent*-**3a**). The enantioselective reaction at λ = 419 nm was performed with 100 µmol **1a** and gave product **3a** (13.2 mg) in 57% yield with 30% *ee*.

4.1.2.5. 2,3,4a,9b-Tetrahydro-2,2,8,9b-tetramethyl-1H-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/Et$_2$O 8:1, CAM) gave the product as a colorless oil (13.2 mg, 54 µmol, 54%). TLC: R_f = 0.33 (P/Et$_2$O 2:1) [CAM]. The spectroscopic data matched the literature values.[2a]

The enantioselective reaction at λ = 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*. $[\alpha]_D^{20}$ = −35.4 (*c* = 0.57, CH$_2$Cl$_2$) [39% *ee*]. Chiral HPLC (OJ-RH, 150 × 4.6 mm, *MeCN* (A)/*H$_2$O* = 20% (A) → 100% (A), 1 mL/min, λ = 210 nm, 254 nm): t_R [racemate] = 14.0 min (**3b**), 15.1 min (*ent*-**3b**). The enantioselective reaction at λ = 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.

4.1.2.6. 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/Et$_2$O 8:1, CAM) gave the product as an orange oil (15.5 mg, 54 µmol, 54%). TLC: R_f = 0.33 (P/Et$_2$O 2:1) [CAM]. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2956 (m, C–H), 1727 (C=O), 1485 (s), 1026 (s), 817 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 0.56 [s, 3H, C-2(CH$_3$)], 1.11 [s, 3H, C-2(CH$_3$)], 1.27 [s, 9H, C(CH$_3$)$_3$], 1.40 [s, 3H, C-9b(CH$_3$)], 1.94 (d, *J* = 14.6 Hz, 1H, C*H*H-1), 2.20 (dd, *J* = 12.8 Hz, *J* = 2.3 Hz, 1H, C*H*H-3), 2.26 (dd,

J = 14.6 Hz, *J* = 2.3 Hz, 1H, CH*H*-1), 2.36 (d, *J* = 12.8 Hz, 1H, CH*H*-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$_{ar}$). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 27.2 [q, C-2(CH$_3$)], 31.8 [q, C(CH$_3$)$_3$], 32.2 [q, C-9b(CH$_3$)], 32.5 [q, C-2(CH$_3$)], 34.5 [s, *C*(CH$_3$)$_3$], 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, C$_{ar}$), 118.8 (d, C$_{ar}$), 125.1 (d, C$_{ar}$), 133.8 (s, C$_{ar}$), 144.6 (s, C$_{ar}$), 155.7 (s, C$_{ar}$), 208.7 (s, C-4). MS (EI, 70 eV): *m/z* (%) = 286 (23) [M$^+$], 271 (100) [(C$_{18}$H$_{23}$O$_2$)$^+$], 173 (24), 153 (53), 57 (48). HRMS (EI, 70 eV): Calculated for C$_{19}$H$_{26}$O$_2$ [M$^+$] = 286.1927. Found = 286.1923.

The enantioselective reaction at λ = 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. [α]$_D^{20}$ = −7.4 (*c* = 0.55, CH$_2$Cl$_2$) [46% *ee*]. Chiral HPLC (AS-RH, 150 × 4.6 mm, *MeCN* (A)/ *H$_2$O* = 20% (A) → 100% (A), 1 mL/min, λ = 210 nm, 254 nm): *t*$_R$ [racemate] = 16.9 min (*ent*-**3c**), 18.2 min (**3c**). The enantioselective reaction at λ = 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.

4.1.2.7. 8-Methoxy-2,2,9b-trimethyl-2,3,4a,9b-tetrahydro-1H-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/Et$_2$O 8:1, CAM) gave the product as a yellow solid (13.0 mg, 50 µmol, 50%). TLC: *R*$_f$ = 0.21 (P/Et$_2$O 2:1) [CAM]. The spectroscopic data matched the literature values.[2a]

The enantioselective reaction at λ = 368 nm was performed with 100 µmol **1d** (irradiation time: 24 h) and gave product **3d** (6.0 mg) in 26% yield with 39% *ee*, 17% r.s.m. [α]$_D^{20}$ = −19.0 (*c* = 0.53, CH$_2$Cl$_2$) [34% *ee*]. Chiral HPLC (AS-RH, 150 × 4.6 mm, *MeCN* (A)/ *H$_2$O* = 20% (A) → 100% (A), 1 mL/min, λ = 210 nm, 254 nm): *t*$_R$ [racemate] = 12.7 min (*ent*-**3d**), 14.3 min (**3d**). The enantioselective reaction at λ = 419 nm was performed with 100 µmol **1d** and gave product **3d** (16.0 mg) in 62% yield with 29% *ee*.

4.1.2.8. 8-Acetyl-2,2,9b-trimethyl-2,3,4a,9b-tetrahydro-1H-dibenzofuran-4-one (rac-3e).
According to the general procedure, compound **1e** (27.2 mg, 100 µmol) was irradiated (irradiation time: 14 h). Purification by column chromatography (pentane/Et$_2$O 2:1, CAM) gave the product as a colorless oil (12.0 mg, 44 µmol, 44%). TLC: *R*$_f$ = 0.34 (P/Et$_2$O 1:2) [CAM]. The spectroscopic data matched the literature values.[2a]

The enantioselective reaction at λ = 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]$_D^{20}$ = −20.7 (*c* = 0.87, CH$_2$Cl$_2$) [27% *ee*]. Chiral HPLC (AD-H, 250 × 4.6 mm, *n*-heptane/*i*-PrOH = 90:10, 1 mL/ min, λ = 210 nm, 254 nm): *t*$_R$ [racemate] = 11.9 min (*ent*-**3e**), 14.3 min (**3e**). The enantioselective reaction at λ = 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.

4.1.2.9. 8-Carbomethoxy-2,2,9b-trimethyl-2,3,4a,9b-tetrahydro-1H-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/Et$_2$O 2:1, CAM) gave the product as a colorless oil (10.7 mg, 37 µmol, 37%). TLC: *R*$_f$ = 0.31 (P/Et$_2$O 1:2) [CAM]. The spectroscopic data matched the literature values.[2a]

The enantioselective reaction at λ = 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. [α]$_D^{20}$ = −31.0 (*c* = 0.65, CH$_2$Cl$_2$) [27% *ee*]. Chiral HPLC (AD-H, 250 × 4.6 mm, *n*-heptane/*i*-PrOH = 90:10, 1 mL/min, λ = 210 nm, 254 nm): *t*$_R$ [racemate] = 9.0 min (*ent*-**3f**), 10.2 min (**3f**). The enantioselective reaction at λ = 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.

4.1.2.10. 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/Et$_2$O 3:2, CAM) gave the product as a white solid (10.3 mg, 40 µmol, 40%). m.p.: 121 °C. TLC: *R*$_f$ = 0.33 (P/Et$_2$O 1:2) [CAM]. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 0.57 [s, 3H, C-2(CH$_3$)], 1.13 [s, 3H, C-2(CH$_3$)], 1.41 [s, 3H, C-9b(CH$_3$)], 2.00 (d, *J* = 14.9 Hz, 1H, C*H*H-1), 2.22−2.26 (m, 2H, CH*H*-1, CH*H*-3), 2.40 (d, *J* = 13.1 Hz, 1H, CH*H*-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$_{ar}$). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 27.0 [q, C-2(CH$_3$)], 32.4 [q, C-2(CH$_3$)], 32.6 [q, C-9b(CH$_3$)], 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*. [α]$_D^{20}$ = −25.9 (*c* = 0.54, CH$_2$Cl$_2$) [30% *ee*]. Chiral HPLC (AD-H, 250 × 4.6 mm, *n*-heptane/*i*-PrOH = 90:10, 1 mL/ min, λ = 210 nm, 254 nm): *t*$_R$ [racemate] = 13.7 min (*ent*-**3g**), 16.7 min (**3g**). The enantioselective reaction at λ = 419 nm was performed with 100 µmol **1g** and gave no product.

4.1.2.11. 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/Et$_2$O 8:1, CAM) gave the product as a colorless solid (15.0 mg, 49 µmol, 49%). m.p.: 86 °C. TLC: *R*$_f$ = 0.33 (P/Et$_2$O 2:1) [CAM]. IR (ATR): ṽ (cm^{-1}) = 2958 (m, C−H), 1722 (s, C=O), 1456 (s), 1180 (s), 1017 (s), 809 (s), 641 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 0.60 [s, 3H, C-2(CH$_3$)], 1.12 [s, 3H, C-2(CH$_3$)], 1.40 (s, 3H, C-9b(CH$_3$)], 1.94 (d, *J* = 14.8 Hz, 1H, C*H*H-1), 2.20−2.24 (m, 2H, CH*H*-1, CH*H*-3), 2.37 (d, *J* = 12.7 Hz, 1H, CH*H*-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$_{ar}$), ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): 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 λ = 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*. [α]$_D^{20}$ = −15.7 (*c* = 0.51, CH$_2$Cl$_2$) [30% *ee*]. Chiral HPLC (AD-H, 250 × 4.6 mm, *n*-heptane/*i*-PrOH = 90:10, 1 mL/ min, λ = 210 nm, 254 nm): *t*$_R$ [racemate] = 10.3 min (*ent*-**3h**), 13.2 min (**3h**). The enantioselective reaction at λ = 419 nm was performed with 100 µmol **1h** and gave product **3h** (12.0 mg) in 39% yield with 30% *ee*.

4.1.2.12. 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/Et$_2$O 8:1, CAM) gave the product as an orange solid (16.0 mg, 57 µmol, 57%). m.p.: 119−121 °C. TLC: *R*$_f$ = 0.41 (P/Et$_2$O 2:1) [CAM]. IR (ATR): ṽ (cm^{-1}) = 2924 (m, C−H), 1715 (s, C=O), 1263 (m), 1028 (s), 804 (s), 744 (m). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 0.64 [s, 3 H, C-10(CH$_3$)], 1.17 [s, 3H, C-10(CH$_3$)], 1.67 [s, 3H, C-11a(CH$_3$)], 2.15 (d,

$J = 14.8$ Hz, 1H, C*H*H-9), 2.31 (dd, $J = 13.6$ Hz, $J = 1.8$ Hz 1H, C*H*H-11), 2.39 (d, $J = 13.6$ Hz, 1H, CH*H*-11), 2.78 (dd, $J = 14.8$ Hz, $J = 1.8$ Hz, 1H, CH*H*-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}). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 27.0 [q, C-10(CH$_3$)], 30.4 [q, C-11a(CH$_3$)], 32.1 [q, C-10(CH$_3$)], 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, C_{ar}), 121.6 (d, C_{ar}), 123.1 (d, C_{ar}), 124.6 (s, C_{ar}), 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) [(C$_{18}$H$_{17}$O$_2$)$^+$], 237 (3) [(C$_{16}$H$_{13}$O$_2$)$^+$], 220 (25), 205 (100), 182 (60), 153 (25), 83 (25). HRMS (EI, 70 eV): Calculated for (C$_{19}$H$_{20}$O$_2$) [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*. [α]$_D^{20}$ = −43.1 ($c = 0.51$, CH$_2$Cl$_2$) [9% *ee*]. Chiral HPLC (OJ-RH, 150 × 4.6 mm, MeCN (A)/H$_2$O = 20% (A) → 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 μmol **1i** and gave product **3i** (16.0 mg) in 57% yield with 9% *ee*.

4.1.2.13. trans-2,2,9b-Trimethyl-2,3,4a,9b-tetrahydro-1H-dibenzo-furan-4-one (rac-5a).
According to the general procedure, compound **1a** (23.0 mg, 100 μmol) was irradiated (irradiation time: 22 h) in dry CH$_2$Cl$_2$. Purification by column chromatography (pentane/Et$_2$O 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, 44 μmol, 44%). TLC: R_f = 0.61 (P/Et$_2$O 2:1) [CAM]. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2928 (m, C–H), 1738 (s, C=O), 1459 (s), 1203 (s), 1044 (s), 748 (s). ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) = 1.14 [s, 3H, C-9b(CH$_3$)], 1.27 [s, 3H, C-2(CH$_3$)], 1.28 [s, 3H, C-2(CH$_3$)], 2.21–2.27 (m, 2H, H-3), 2.46 (dd, $J = 18.1$ Hz, $J = 1.0$ Hz, 1H, C*H*H-1), 2.55 (d, $J = 18.1$ Hz, 1H, CH*H*-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}). ^{13}C {^{1}H} NMR (126 MHz, CDCl$_3$): δ (ppm) = 23.0 [q, C-9b(CH$_3$)], 34.6 [q, C-2(CH$_3$)], 34.7 (s, C-2), 36.3 [q, C-2(CH$_3$)], 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) [(C$_{14}$H$_{15}$O$_2$)$^+$], 173 (42) [(C$_{11}$H$_{19}$O$_2$)$^+$], 145 (40), 131 (99), 83 (100). HRMS (EI, 70 eV): Calculated for (C$_{15}$H$_{18}$O$_2$) [M$^+$] = 230.1301. Found: 230.1296.

4.1.3. Syntheses of compounds 6-8
4.1.3.1. 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-propanol[31] (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 NaHCO$_3$-solution and brine, dried over Na$_2$SO$_4$ 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_f = 0.18 (EtOAc) [KMnO$_4$]. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2894 (w, C–H), 1650 (s, C=N), 1510 (s), 1240 (s), 730 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.45 [s, 6H, (CH$_3$)$_2$], 2.61 (dd, $J = 13.8$ Hz, $J = 8.4$ Hz, 2H, 2 × C*H*HPh), 3.01 (dd, $J = 13.8$ Hz, $J = 4.7$ Hz, 2H, 2 × CH*H*Ph), 3.99 (dd, $J = 8.4$ Hz, $J = 6.9$ Hz, 2H, 2 × OC*H*H), 4.16 (dd, $J = 9.2$ Hz, $J = 8.4$ Hz, 2H, 2 × OCH*H*), 4.32–4.40 (m, 2H, 2 × CH), 5.03 (s, 4H, 2 × OCH$_2$Ph), 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}). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 24.4 (q, [C(CH$_3$)], 38.7 [s, C(CH$_3$)$_2$], 40.5

(t, CH$_2$Ph), 67.3 (d, CH), 70.2 (t, OCH$_2$Ph), 72.1 (t, OCH$_2$), 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 C$_{37}$H$_{39}$N$_2$O$_4$ [(M+H)$^+$] = 575.2865. Found = 575.2908.

4.1.3.2. 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-3-methylcyclohexanone[32] (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$_2$Cl$_2$ and water. After separation of the layers, the aqueous phase was extracted three times with CH$_2$Cl$_2$ (15 mL). The combined organic phases were washed with brine (60 mL), dried over Na$_2$SO$_4$ and filtered. After evaporation the crude material was purified by column chromatography (pentane/Et$_2$O 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/Et$_2$O 2:1): R_f = 0.29 [UV, CAM]. IR (ATR): $\tilde{\nu}$ (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). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.93 (s, 3H, CH$_3$), 2.07–2.13 (m, 2H, CH$_2$), 2.55–2.58 (m, 4H, 2 × 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}). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 18.1 (q, CH$_3$), 22.2 (t, CH$_2$), 31.8 (t, CH$_2$), 38.5 (t, CH$_2$), 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 - CH$_3$)$^+$], 174 (21) [(C$_{11}$H$_{10}$O$_2$)$^+$], 159 (13) [(C$_{10}$H$_7$O$_2$)$^+$], 145 (20) [(C$_9$H$_5$O$_2$)$^+$], 77 (15) [(C$_6$H$_5$)$^+$]. HRMS (EI, 70 eV): Calculated for C$_{13}$H$_{14}$O$_2$ [M$^+$] = 202.0988. Found = 202.0983.

4.1.3.3. 3-(4-Pentenyl)-2-phenoxy-2-cyclohexen-l-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 μL, 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 Et$_2$O (3 × 10 mL). The combined organic layers were washed with brine (35 mL), dried over Na$_2$SO$_4$ and filtered. After evaporation the crude material was purified by column chromatography (pentane/Et$_2$O 10:1, UV, CAM) gave the product as a yellow oil (618 mg, 2.41 mmol, 69%). TLC: R_f = 0.48 (P/Et$_2$O 1:1) [UV, CAM]. The spectroscopic data matched the literature values.[4c]

4.1.3.4. 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/Et$_2$O 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/Et$_2$O 2:1) [CAM]. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2965 (w, C–H), 2929 (w, C–H), 1719 (m, C=O), 1472 (m), 1459 (m), 1027 (m), 740 (s), 752 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.44 (s, 3H, CH$_3$), 1.63–1.73 (m, 1H, C*H*H-2), 1.83 (t, $J = 13.3$ Hz, 1H, C*H*H-1), 1.86–1.96 (m, 1H, CH*H*-2), 2.03–2.06 (m, 1H, CH*H*-1), 2.32–2.40 (m, 1H, C*H*H-3), 2.54–2.58 (m, 1H, CH*H*-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}). ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 20.8 (t, C-2), 28.2 (q, CH$_3$), 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) [$(C_{12}H_{11}O_2)$], 159 (24) [$(C_{10}H_7O_2)^+$], 145 (95) [$(C_9H_5O_2)^+$], 131 (100), 77 (18) [$(C_6H_5)^+$]. HRMS (EI, 70 eV): Calculated for $(C_{13}H_{14}O_2)$ [M$^+$] = 202.0988. Found: 202.0985.

The enantioselective reaction at $\lambda = 368$ nm was performed with 100 μmol **7a** (irradiation time: 24 h) and gave product **8** (13.9 mg) in 69% yield with 20% *ee*. $[\alpha]_D^{20} = -9.9$ ($c = 0.41$, CH$_2$Cl$_2$) [20% *ee*]. Chiral HPLC (AS-RH, 150 × 4.6 mm, *MeCN* (A)/H_2O = 20% (A) → 100% (A), 1 mL/min, $\lambda = 210$ nm, 254 nm): t_R [racemate] = 11.9 min (*ent*-**8**), 12.6 min (**8**).

*4.1.3.5. 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/Et$_2$O 10:1, CAM) gave the product as a yellow oil (20.0 mg, 78 μmol, 78%). TLC: R_f = 0.66 (P/Et$_2$O 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_2O = 20% (A) → 100% (A), 1 mL/min, $\lambda = 210$ nm, 254 nm): t_R [racemate] = 19.6 min, 20.4 min.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2017.05.005.

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