

Photocatalytic tetrapeptides for enantioselective visible light-induced transformations

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Research on enantioselective photocatalysis has so far been focused on molecular photocatalysts or large yet easily adaptable photoenzymes. However, both catalysis classes display deficiencies either due to their limited adaptability or their high molecular weight. Here we show that small peptides can bridge the gap between the currently used photocatalysts by combining structural flexibility and low molecular weight. We constructed a small peptide that displays a pyroglutamic acid at its N terminus for substrate recognition. At the C terminus, a thioxanthone-based amino acid was installed to harvest photons and to act catalytically by energy transfer. Two amino acids were sufficient to link the two components, resulting in a photocatalytically active tetrapeptide that was used both for photochemical deracemization and enantioselective [2 + 2] photocycloaddition reactions. Our results demonstrate that small peptides with a molecular weight below 750 Da can act as efficient molecular catalysts for enantioselective photochemical transformations.

One of the greatest and most comprehensive challenges of contemporary chemical synthesis pertains to the construction of chiral molecules in an enantioselective fashion¹. Driven by the needs of the life science industry, the market for enantiomerically pure compounds is rapidly growing and requires a continuous influx of new methods^{2,3}. In the past two decades, photochemistry has established itself as a key technology to access new structure classes and to streamline synthetic procedures. Ultraviolet (UV) (wavelength λ = 250–380 nm) or visible light (λ = 380–750 nm) irradiation triggers photochemical reactions by promoting a given substrate from the ground state (S_0) to a higher excited state. While the population of excited states is the hallmark of photochemistry, the high energy input, typically >200 kJ mol⁻¹, poses a substantial challenge as far as enantioselectivity is concerned. The conventional mode of action for enantioselective catalysis relies on the lowering of activation barriers and is not applicable to photochemical

transformations, which often occur almost barrierless. A chiral catalyst must therefore interact with a photochemical substrate before it is promoted to the excited state^{4–7}. In this vein, triplet energy transfer (sensitization) from a catalytically active compound to the substrate represents a possible solution for enantioselective photocatalysis⁸ (Fig. 1). Suitable catalysts display an energetically high lying triplet state T_1 that is populated by rapid intersystem crossing after direct excitation to an excited singlet state (S_n). Although the idea of enantioselective catalysis by sensitization dates to the 1970s^{9,10}, the first catalyst to provide high catalytic activity and high enantioselectivity was chiral xanthone **1**, first disclosed in 2009¹¹. Here a lactam binding motif recruits the substrate and ensures that the substrate molecule remains in the chiral environment of the catalyst after energy transfer. Other small chiral molecules, for example, **2**¹² and **A-3**¹³, have emerged and have been found to exhibit similar catalytic properties (Fig. 1b).

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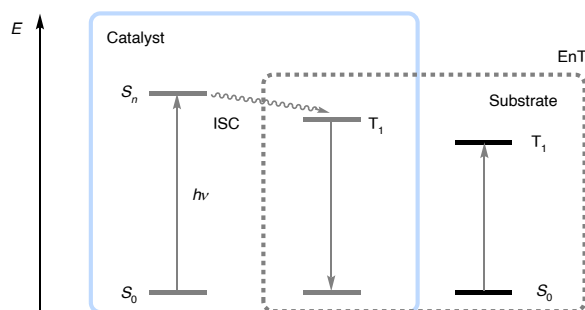
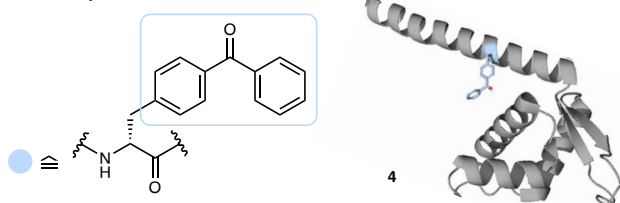
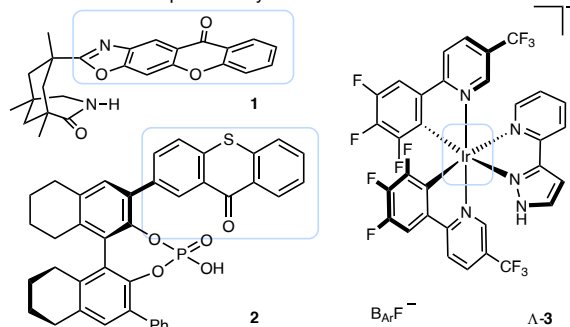
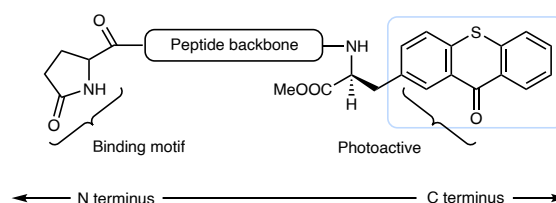
a Photocatalysis by triplet energy transfer (EnT)**c** Photoenzymes

Fig. 1 | Approaches towards enantioselective catalysis in photochemistry by energy transfer from a chiral catalyst. **a**, Energy transfer from a catalyst promotes the substrate to its reactive first excited triplet state T_1 (S_0 , ground state; S_n , higher excited state; EnT, energy transfer). **b**, Molecular catalysts combine a binding motif with a photochemically active entity. They can be highly selective, but any optimization requires extensive synthetic work. **c**, Photoenzymes can be readily optimized towards a given substrate class by

b Chiral molecular photocatalysts**d** Concept for a peptidic photocatalyst

directed evolution. However, a large framework (>20 kDa) is required to position a single photocatalytically active chromophore (here a benzophenone)¹⁹, limiting the quantum efficiency per mass. **d**, Small peptides with a molecular weight below 1 kDa offer high substrate specificity and an adjustment of the backbone to a given substrate class. In the present study, a suitable peptide backbone was to be identified to connect an N-terminal Pga and a C-terminal pTxa. *h*, Planck's constant; ISC, intersystem crossing; ν , frequency of light.

The advent of genetic code expansion¹⁴ and of directed evolution¹⁵ has, in the past five years, led to a rapid growth of photoenzymes^{16,17} that can catalyse photochemical reactions enantioselectively by triplet energy transfer. In pioneering work by Green¹⁸ and colleagues and Chen, Zhong, Wu¹⁹ and colleagues, *para*-benzoyl-substituted phenylalanine was incorporated into existing enzyme scaffolds, for example, **4** (Fig. 1c), and the resulting proteins were further optimized towards [2 + 2] photocycloaddition reactions. While the *para*-benzoyl-substituted phenylalanine chromophore requires UV irradiation for optimum performance, very recent work has shown that thioxanthone-substituted amino acids can also be incorporated^{20–22} and enable photochemical transformations by visible light.

Although both approaches to enantioselective catalysis have their merits, there are also drawbacks. Molecular photocatalysts are typically not synthesized modularly and any modification requires substantial synthetic effort. Photoenzymes are built from a choice of mutually exchangeable amino acids but need to be tailored to a given substrate class, with the adaptation requiring a major screening effort. Their large molecular weight and limited solubility in organic solvents require sophisticated techniques for handling and substrate isolation on a large scale. In addition, the incorporation of noncanonical amino acids as catalytic entities is not trivial and involves complex bioengineering¹⁴. Against this background, it seemed warranted to study small peptides as possible energy transfer catalysts. This compound class has drawn enormous attention in the field of organocatalysis, and many thermal reactions have been reported to occur enantioselectively upon peptide catalysis^{23–25}. Studies with photochemically active peptides are surprisingly rare, although the modularity of their structure promises a facile modification and they are typically soluble in organic solvents. Pioneering work by Wagenknecht and co-workers has revolved around the use of a peptide with an N-terminal arginine and a C-terminal pyrene²⁶ or perylene-substituted²⁷ alanine. The compounds showed

photocatalytic activity in the methanol addition to styrene derivatives acting by single-electron oxidation of the olefinic double bond. However, no enantioselectivities were reported. More recently, small peptides with an N-terminal cysteine have been employed for hydrogen atom transfer to photochemically generated radicals, either in the context of photochemical deracemization^{28,29} or enantioselective hydrodifluoroalkylation reactions³⁰.

Results and discussion

Catalyst discovery and optimization

Our design concept focused on the idea of placing an amino acid with an appropriate motif for substrate recognition on the N-terminal position of a given peptide (Fig. 1d). At the C-terminal position, a thioxanthone was to be responsible for harvesting visible-light photons and for an energy transfer to the substrate. The connecting peptide backbone could be chosen freely and offered an option for optimizing the enantioselectivity. For the present proof-of-concept study, we targeted lactams as possible substrates, which is why a pyroglutamic acid (Pga) was chosen as the N-terminal amino acid. Preliminary experiments were inspired by the work of Wennemers and co-workers on catalytic tripeptides³¹ and of the Miller group on catalytic tetrapeptides³². The photochemical deracemization of allene *rac*-**5a**³³ was chosen as the test reaction. The success of a deracemization³⁴ depends on a differentiation between the two substrate enantiomers **5a** and *ent*-**5a**. Only if the sensitizing entity, here the C-terminal thioxanthone, gets into close contact with the substrate is energy transfer possible and an achiral intermediate forms, which reforms either one of the enantiomers **5a** or *ent*-**5a**. If one of the enantiomers is preferably processed, the other enantiomer is enriched in the photostationary state. The reaction, thus, serves as a useful probe to interrogate the distance between the C-terminal chromophore and the N-terminally bound substrate. In random screening experiments, it was found that a two amino acid

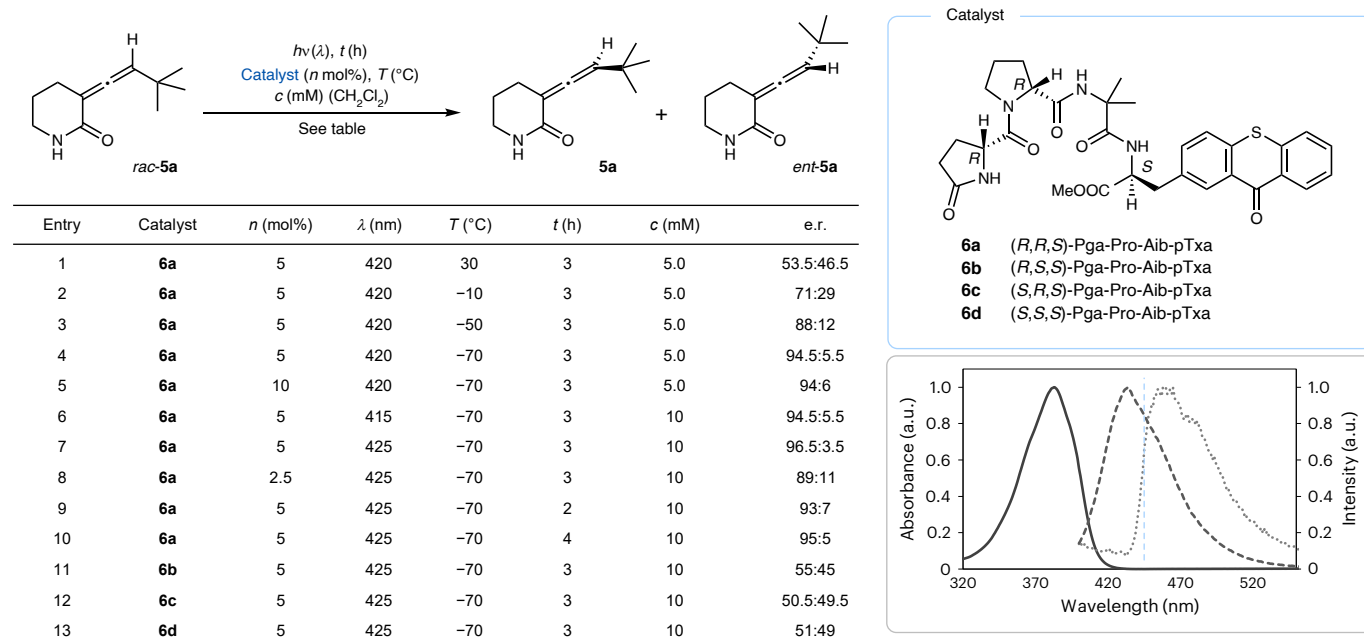


Fig. 2 | Deracemization of chiral allene *rac*-5a** by a small peptide photocatalyst upon irradiation with visible light.** Preliminary screening results were performed on a 30- μ mol scale. The enantiomeric ratio (e.r.) was determined by chiral high-performance liquid chromatography (HPLC) analysis. Photophysical properties are provided for peptide **6a** and were determined in

EtOH solution. From the inflection point (indicated by the dashed blue line) of the phosphorescence spectrum (77 K, EtOH) the triplet energy was calculated as 269 kJ mol⁻¹. Solid line (—), UV/Vis spectrum; dashed line (---), luminescence spectrum; dotted line (····), phosphorescence spectrum (77 K); *c*, concentration; *t*, time; *T*, temperature. Source data

β -turn-inducing motif (*vide infra*) consisting of proline (Pro) and achiral aminoisobutyric acid (Aib), as previously utilized by Miller^{25,32}, is sufficient to deliver a catalyst that displays a notable enantioselectivity. The C-terminal carboxylic acid 9-oxothioxanthene-2-yl-substituted alanine (pTxa) was prepared from (S)-serine and was used consistently with this configuration³⁵. With three stereogenic centres present, there are four diastereoisomers of tetrapeptide **6**, all of which were prepared and evaluated in the deracemization reaction (Fig. 2).

The reactions were performed with dichloromethane as the solvent, with light sources emitting at a maximum of $\lambda = 420$ nm (fluorescent lamps), $\lambda = 415$ nm (light-emitting diode (LED)) or $\lambda = 425$ nm (LED). At ambient temperature, peptide **6a** provided almost no preference towards one enantiomer and the enantiomeric ratio (e.r.) in favour of enantiomer **5a** was low (Fig. 2, entry 1). However, upon decreasing the temperature, the e.r. continuously increased (entries 2–4), reaching a value of 94.5:5.5 at temperature $T = -70$ °C. An increase in catalyst loading was not beneficial to the enantioselectivity (entry 5). Under the conditions of entry 4, other solvents were screened (see Supplementary Table 2 for full details on the optimization studies), but they turned out to be inferior to dichloromethane. Employing an LED in a different set-up allowed us to irradiate a more concentrated solution and resulted in a lower e.r. at $\lambda = 415$ nm (entry 6) and an improvement of the e.r. (entry 7) at $\lambda = 425$ nm. Under the latter conditions, we checked whether a lower catalyst loading (entry 8) or a change of the irradiation time (entries 9 and 10) led to a better e.r., which turned out not to be the case. Under the conditions of entry 7, a preparative run delivered allene **5a** in quantitative yield (>99%) with an e.r. of 96:4. Remarkably, all other diastereoisomers of peptide **6** performed poorly in the deracemization reaction (entries 11–13), underscoring the relevance of the peptide backbone for the enantioselectivity. The prominent photophysical characteristics of catalyst **6a** (absorption and luminescence) are due to the thioxanthone embedded in pTxa and are comparable to parent 9H-thioxanthene-9-one³⁶. The longest wavelength absorption was found at $\lambda = 383$ nm (molar decadic absorption coefficient $\epsilon = 5,700$ M⁻¹ cm⁻¹) and the triplet energy was determined as $E_T = 269$ kJ mol⁻¹.

NMR spectroscopy studies and molecular dynamics simulations

The remarkable success of peptide diastereoisomer **6a** prompted a more detailed investigation of its conformation and its binding to the allene enantiomers **5a** and *ent*-**5a** (Fig. 3). Thus, we conducted a set of nuclear magnetic resonance (NMR) spectroscopy experiments at 233 K for resonance assignment and the extraction of distance information resulting in the collection of 33 distance restraints for the peptide **6a** (Fig. 3a and Supplementary Table 1). These restraints were used for structure calculation yielding a well-defined structural ensemble with a root mean square deviation (r.m.s.d.) for heavy atoms of 0.22 Å (Fig. 3b). The tetrapeptide adopts a type II' β -turn conformation^{32,37}, a structural motif that has been previously observed in cyclic peptides following a (R)-proline residue³⁸ and also in acyclic peptides with an (R)-Pro-Aib substructure^{32,39}. In this β II' turn the existence of a hydrogen bond between the amide proton of pTxa and the backbone carbonyl of Pga is evident from specific rotating-frame nuclear Overhauser effect restraints (Fig. 3a) between the two residues and a temperature coefficient⁴⁰ of -4.7 ppb K⁻¹ for the amide of pTxa (Supplementary Fig. 8). The photoactive thioxanthone ring is located above the β -turn structure in a tilted orientation.

The addition of the substrate *ent*-**5a** selectively induced strong amide chemical shift perturbations within the pyroglutamate ring of **6a** (Fig. 3c). The binding site in *ent*-**5a** for **6a** was identified by the strong NMR spectroscopy chemical shift perturbation of its lactam HN moiety in the complex (Fig. 3c). Furthermore, we observed nuclear Overhauser effect contacts between the H^N atoms of both components (Supplementary Fig. 9 and Supplementary Table 1). This information was used for a structure calculation of the complex resulting in a structural bundle with a heavy atom r.m.s.d. of 1.14 Å (Fig. 3d). In this structure, *ent*-**5a** binds to the lactam ring of Pga in **6a** via two hydrogen bonds, placing the substituents of the allene in a sterically favourable orientation with the *tert*-butyl moiety facing away from the thioxanthone ring, enabling proximity (approximately 4 Å) of the allene and the aromatic ring system of the peptide photocatalyst. In contrast,

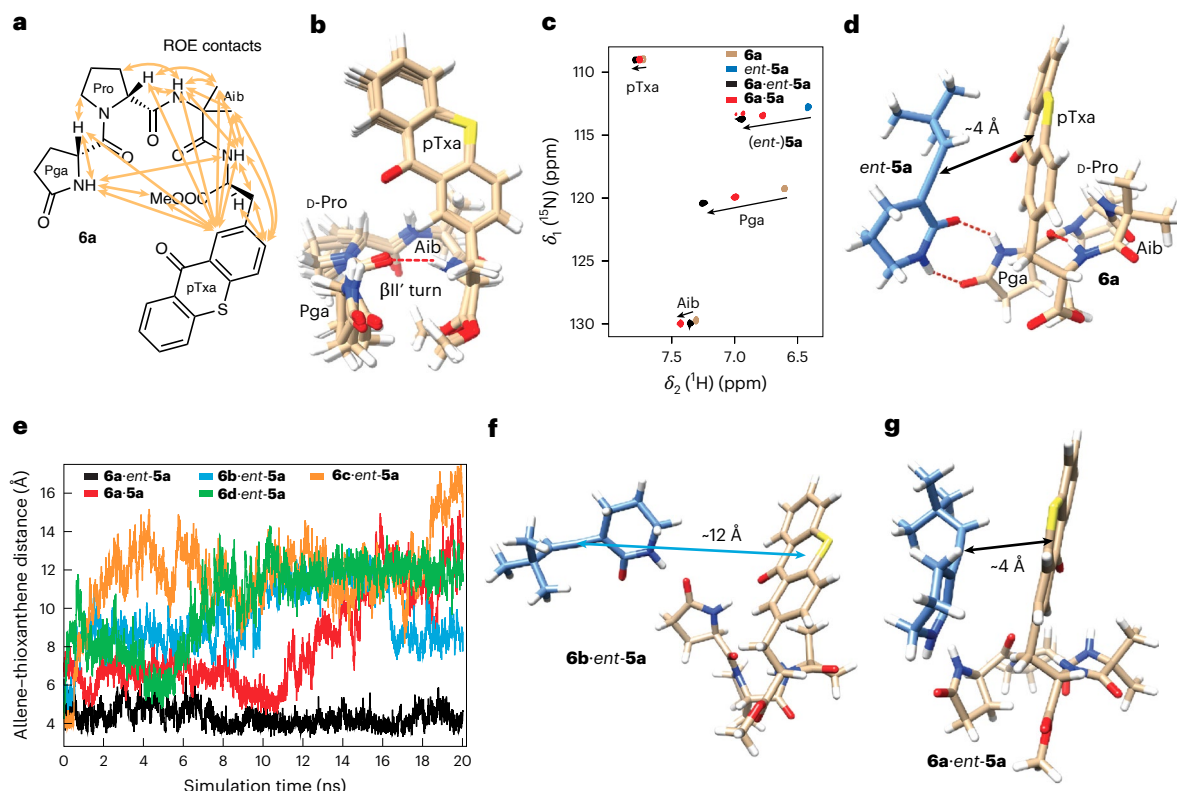


Fig. 3 | Structural characterization of the photocatalytic peptide 6a and its complex with *rac*-5a by NMR spectroscopy and molecular dynamics simulations. **a**, Rotating-frame nuclear Overhauser effect (ROE)-derived distance restraints for peptide 6a. **b**, Structural bundle of 6a with a heavy atom r.m.s.d. of 0.22 Å indicating a β II'-turn conformation. **c**, Two-dimensional-NMR spectroscopy titration experiments with 6a and *ent*-5a or 5a indicating binding between the lactam moieties of both components, with stronger effects observed for *ent*-5a. **d**, Structure of complex 6a-*ent*-5a reveals a binding mode that provides proximity (approximately 4 Å) between the allene and the

photoactive thioxanthone ring. **e**, Distance versus simulation time for compound *ent*-5a in complex with tetrapeptide 6a (black curve); the allene enantiomer 5a in complex with 6a (red curve); and *ent*-5a in complex with 6b (blue curve), 6c (orange curve) and 6d (green curve). **f**, Snapshot of a nearly dissociated state with an allene–thioxanthone distance of approximately 12 Å for complex 6b-*ent*-5a. **g**, Typical arrangement of *ent*-5a stacking on the thioxanthone ring of 6a observed as dominant state during the simulation of the 6a-*ent*-5a complex (allene–thioxanthone distance of approximately 4 Å). Source data

enantiomer 5a induced lower chemical shift perturbations than *ent*-5a, indicating weaker binding (Fig. 3c). Multiple molecular dynamics simulations were started from the NMR spectroscopy-derived structure of complex 6a-*ent*-5a (Fig. 3e). In most simulations, the geometry stayed close to the NMR spectroscopy structure during the 20 ns simulation time, with a distance of approximately 4 Å between the central carbon atom of the allene and the thioxanthone ring in the peptide (Fig. 3d,g). The short allene–thioxanthone ring distance represents approximately the sum of the van der Waals radii, allowing efficient energy transfer⁴¹ and photocatalysis. In addition to simulations on complex 6a-*ent*-5a, molecular dynamics simulations were also performed with complex 6a-5a. The starting structures were otherwise kept as close as possible to the NMR spectroscopy-based structure 6a-*ent*-5a to allow for a close initial contact between allene and the thioxanthone ring (Fig. 3e). However, in this case, even in the starting structure, the smallest distance that was sterically possible without disrupting the hydrogen bonds between peptide and substrate was larger than 5 Å. In all simulations the contact was lost rapidly and the substrate 5a frequently dissociated within a few nanoseconds (Fig. 3e; for results of additional simulations, see also Supplementary Fig. 10). In all simulations for peptides 6b–6d with altered chirality at the Pga ring or the Pro residue, a close allene–thioxanthone distance was sterically not possible in the starting structure (without disruption of hydrogen bonds) and/or a rapid rearrangement and dissociation occurred within a few nanoseconds simulation time (Fig. 3e,f and Supplementary Fig. 10). The simulations demonstrate that a close distance between the allene group and

thioxanthone only appears sterically possible and stable for complex 6a-*ent*-5a (Fig. 3g). In all other cases, a close contact geometry and simultaneous stabilization by hydrogen bonding between allene and tetrapeptide are sterically not possible, resulting in rapid dissociation.

Applications in deracemization and [2 + 2] photocycloaddition

The NMR spectroscopy and molecular dynamics studies support the idea that peptide 6a is suitable for use in differentiating between allene isomers 5a and *ent*-5a. Upon excitation of the thioxanthone within pTxa, energy transfer occurs mainly to enantiomer *ent*-5a, which undergoes racemization via an achiral intermediate. As binding of enantiomer 5a to catalyst 6a is strongly attenuated and kinetically unstable, it is not processed, or is only slowly processed, and prevails in the photostationary state. Related deracemization reactions were attempted with other allenes *rac*-5 (Fig. 4), and it was found that the enantioselectivity remains high (products 5b and 5g–5m) with tertiary substituents at the terminal allene carbon atom. Once the size of the substituent was decreased, the enantioselectivity also decreased and the e.r. went down to 90:10 for secondary and primary substituents (products 5c–5e) and to 83:17 for the methyl-substituted allene 5f. In these cases, it turned out to be beneficial to use the difluoro analogue 7a of tetrapeptide 6a as the catalyst. Our rationale for the introduction of the fluorine atoms was to increase the strength of the hydrogen bonding event and, thus, to improve the differentiation between the allene enantiomers. By doing so, products 5c–5e were accessible

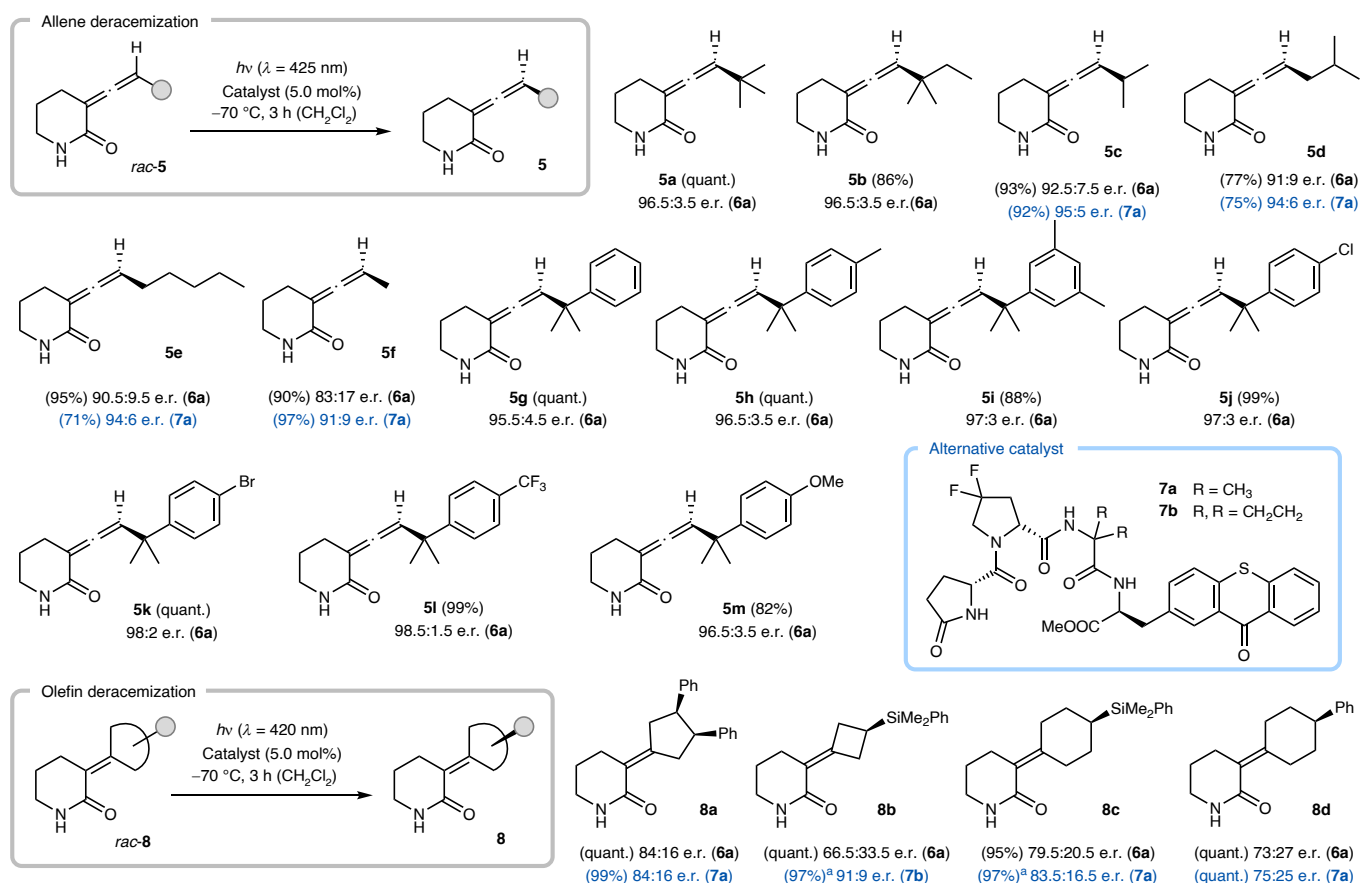


Fig. 4 | Deracemization of chiral allenes *rac*-5 and chiral olefins *rac*-8 catalysed by peptidic catalysts. Substrates were irradiated at -70°C in the presence of peptide catalysts **6a** or **7** for the indicated time period and at the

indicated wavelength in dichloromethane solution ($c = 10 \text{ mM}$, $30\text{-}\mu\text{mol}$ scale). Enantiomeric ratios were determined by chiral HPLC analysis. Yields refer to isolated product. $^a\lambda = 425 \text{ nm}$. quant., quantitative yield.

in an e.r. of 94:6 or higher, and even the methyl-substitute allene **5f** displayed an e.r. of 91:9. The aryl-substituted allenes **5g–5m** reacted smoothly (82% to quantitative yield) and with high enantioselectivity (95:5 to 98:2 e.r.) in the presence of tetrapeptide **6a**. Functional group tolerance was established for halogen (**5j** and **5k**), trifluoromethyl (**5l**) and methoxy (**5m**) substituents. The results align with previous work^{11,36} that has established the remarkable compatibility of the thioxanthone chromophore with a variety of substituents in photochemical reactions. Catalyst recovery is possible and was performed in a 0.24-mmol experiment, in which product **5a** was obtained in quantitative yield (96:4 e.r.). After column chromatography, 70% of catalyst **6a** was re-isolated.

Tetrasubstituted alkylidenecycloalkanes *rac*-8 represent another class of chiral compounds that have been shown to be of high relevance^{42,43}, and that can be deracemized photochemically^{44,45}. Here energy transfer to the olefin leads to a rotation around the former double bond and the triplet $\pi\pi^*$ state is achiral. Upon returning to the ground state hypersurface, the double bond is restored, leading to a racemization. Like for allenes *rac*-5, the key challenge is the distinction between the two substrate enantiomers **8** and *ent*-8. For the olefin deracemization, peptide catalyst **7** turned out to be consistently superior to catalyst **6a**, and their facile synthesis is testimony to the benefit of a modular design. The enantioselectivities for cyclopentane **8a** and cyclobutane **8b** were high, and even for the 4-monosubstituted cyclohexanes **8c** and **8d**, a notable enantioselectivity was recorded.

In a final synthetic study, we explored the potential of peptidic catalyst **6a** in enantioselective photocycloaddition reactions. Specifically, the intramolecular [2 + 2] photocycloaddition of quinolones **9**

was chosen, which had been previously studied both with a molecular thioxanthone catalyst⁴⁶ and with photoenzymes^{19,22}. Gratifyingly, we found the peptidic catalyst to be equally efficient in the conversion **9** → **10**, which proceeded in high yields (77% to quantitative yield) and enantioselectivities ranging from 89:11 to 99:1 e.r. (Fig. 5).

The reaction was not stereospecific and products **10c** were obtained with a diastereomeric ratio of 76:24. This outcome is in line with the postulated triplet pathway along which the reaction progresses. In fact, we suppose that in analogy to alkene *ent*-5a, the substrate **9** of the reaction binds to the N-terminal amino acid Pga by two-point hydrogen bonding. Upon excitation, the thioxanthone at the C-terminal amino acid is ideally positioned to promote the quinolone into its triplet state by energy transfer. In addition, it shields one of the two enantiotopic faces of the quinolone, and intermolecular attack of the olefin occurs with high enantioselectivity at carbon atom C4. The ensuing triplet 1,4-diradical allows for rotation around the C–C bond, which explains the observed non-stereospecific reaction course. After intersystem crossing, ring closure occurs, yielding the desired cyclobutane products. As the quinolones do not absorb at $\lambda = 425 \text{ nm}$, there is no racemic background reaction.

Conclusion

Small peptidic catalysts with a C-terminal sensitizing amino acid (pTx) have been introduced as a new class of catalysts for photochemical transformations. Upon proper adjustment of the two amino acids in the backbone, the N-terminal amino acid Pga is optimally positioned for recruitment of a given photochemical substrate. The three-dimensional structure of the complex has been established by NMR spectroscopic

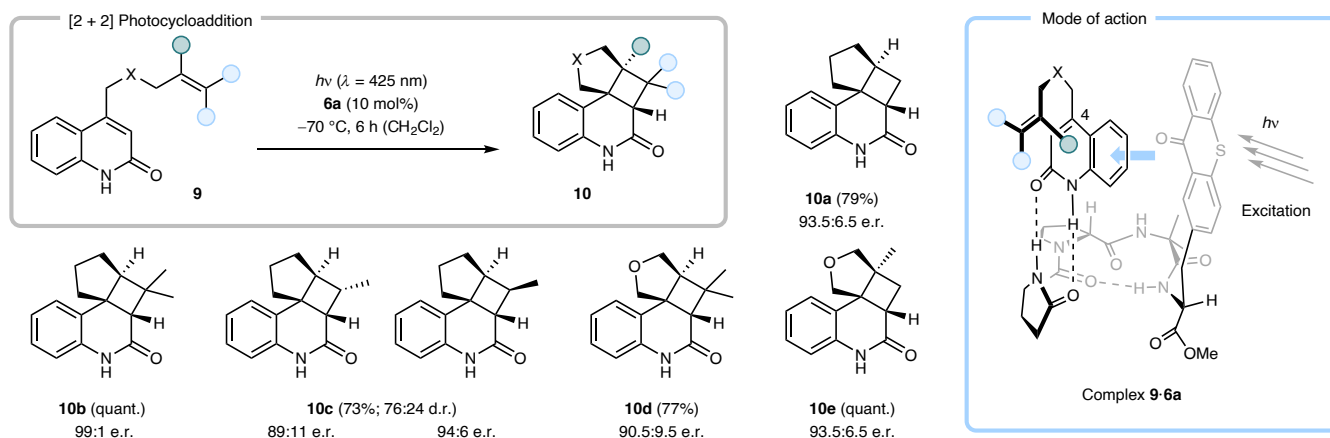


Fig. 5 | Enantioselective intramolecular [2 + 2] photocycloaddition reactions promoted by catalyst **6a.** The substrates were irradiated for 6 hours at a wavelength of $\lambda = 425$ nm and at a temperature of -70 °C in dichloromethane solution ($c = 5$ mM, 30- μmol scale). Enantiomeric ratios were determined by chiral HPLC analysis and diastereomeric ratios (d.r.) by ^1H -NMR spectroscopy

integration. Yields refer to isolated product. A hydrogen-bonded complex of the substrate **9** to the catalyst is postulated in which energy transfer is possible and in which the approach of the olefin can occur only from one face relative to carbon atom C4.

analysis, and the relevance of the chiral backbone for substrate binding was demonstrated by molecular dynamics calculations. The parallel alignment of catalytically active chromophore and substrate allows for several enantioselective transformations to be performed in high yields and with excellent enantioselectivity. Unlike for molecular catalysts, the synthesis of the peptidic catalysts is modular and allows for a wide modification employing the wide pool of amino acids. The study provides proof of concept for the suitability of peptidic photocatalysts in the emerging field of enantioselective photocatalysis. We anticipate that our current design will be the starting point for the development of more sophisticated small peptides applicable to a wide set of diverse photochemical reactions.

Methods

Photochemical deracemizations of allenes *rac*-**5**

A dried LED tube was charged with the respective allene *rac*-**5** (30.0 μmol , concentration $c = 10$ mM, 1.00 equiv.) and thioxanthone catalyst **6a** or **7a** (1.50 μmol , 5.0 mol%) under argon atmosphere, followed by the addition of dry, deaerated CH_2Cl_2 (3.00 ml). The resulting solution was irradiated with an LED ($\lambda_{\text{max}} = 425$ nm) at -70 °C for 3 hours. The reaction mixture was concentrated under reduced pressure and the crude products were subsequently purified by flash column chromatography (SiO_2 , EtOAc/methanol) to yield the enantioenriched allenes **5** as colourless solids (Fig. 4).

Enantioselective [2 + 2] photocycloadditions of quinolones **9**

A dried LED tube was charged with the respective quinolone **9** (30.0 μmol , $c = 5.0$ mM, 1.00 equiv.) and thioxanthone catalyst **6a** (1.82 mg, 3.00 μmol , 10 mol%) under argon atmosphere, followed by the addition of dry, deaerated CH_2Cl_2 (6.00 ml). The resulting solution was irradiated with an LED ($\lambda_{\text{max}} = 425$ nm) at -70 °C for 6 hours. The reaction mixture was concentrated under reduced pressure and the crude products were subsequently purified by flash column chromatography (SiO_2 , EtOAc/pentane) to yield the enantioenriched quinolones **10** as colourless solids (Fig. 5).

Data availability

The data that support the findings of this study are available in the Supplementary Information, including detailed experimental procedures, materials and methods, characterization data for new compounds, details and supplementary results of the NMR spectroscopy investigations and molecular dynamics simulations, extended

screening tables, NMR spectra for new compounds, chiral HPLC traces, Supplementary Figs. 1–10 and Supplementary Tables 1–4. Primary research data are openly available in the Chemotion Repository at https://doi.org/10.14272/collection/RMI_2026-01-30. Source data are provided with this paper.

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Author contributions

R.M.I. discovered and optimized catalyst **6a** and carried out the experiments illustrated in Figs. 2 and 4 (allene deracemization) and Fig. 5. I.L. performed the synthesis of catalyst **7** and the experiments illustrated in Fig. 4 (olefin deracemization). F.H. performed the NMR spectroscopy studies on the peptide and M.Z. the molecular dynamics calculations. T.B. directed the project. All authors contributed to the data analysis and the writing of the paper.

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Competing interests

The authors declare no competing interests.

Additional information

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