

Photochemical and Photocatalytic Deracemization Reactions

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Abstract:

Under photochemical conditions and using an appropriate chiral catalyst, racemic mixtures of compounds can convert to enantioenriched mixtures through distinguished pathways which are called photochemical and photocatalytic deracemization reactions.

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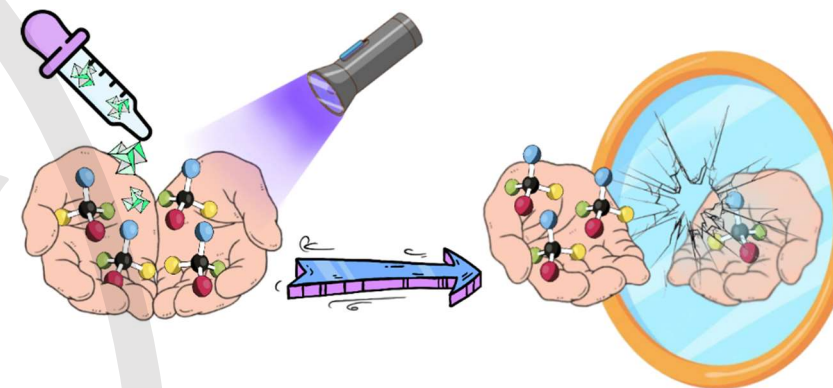
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Photochemical and Photocatalytic Deracemization Reactions

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Abstract Under photochemical conditions and using an appropriate chiral catalyst, racemic mixtures of compounds can convert to enantioenriched mixtures through distinguished pathways which are called photochemical and photocatalytic deracemization reactions.

Key words photochemical deracemization, chiral compounds, enantioenrichment, photocatalyst, photoredox

For many years, the resolution of racemic mixtures into their constituent enantiomers has been a critical area of research for chemists. The valuable applications and advanced properties of enantiomerically pure compounds for pharmaceuticals, catalysis, and materials, in comparison with their racemates, is one of the main reasons for this pursuit which obviously leads chemists toward new pathways and conditions, aiming to enhance the efficiency of deracemization reactions.

In this graphical review, we have focused on photochemical deracemization reactions which occur using light as the critical element and utilizing suitable chiral photocatalysts. Due to high-atom economy and efficient enantioenrichment of photocatalytic deracemization reactions in most cases, it has been a preferable way between other methods of deracemization reactions.

Photons and chiral photocatalysts, as major parts of these reactions, can make specific stereocenters of racemic compounds editable. This phenomenon happens by utilization of light to overcome thermodynamic constraints. Furthermore, chiral photocatalyst cooperates with photons and facilitates the way for molecules to reach the excited state which includes planar intermediates. The plateau of excited state is also capable of inhibiting microscopic reversibility, which is a serious kinetic obstacle in

deracemization reactions. On the next step, according to the certain mechanism of the reaction, the achiral intermediate can convert into both enantiomers, with the fact that the formation of one enantiomer is favorable over the other.

Considerable advancements have occurred in the field of photochemical and photocatalytic deracemization over the past few years. In this review, we have attempted to compile these studies and some early reports on photochemical deracemization and organize the topic into comprehensible classifications. Therefore, we have classified the photochemical deracemization reactions into two major categories based on their two different mechanisms: Energy-Transfer-Based (EnT) photocatalysis and Photoredox catalysis. Consequently, each substrate is divided according to the photocatalyst applied.

In EnT based photocatalysis, chiral photocatalysts can interact with each enantiomer in different way to make the stereoablative step that involves a prochiral intermediate which is subsequently re-converted via an enantioselective transformation. Generally, the major enantiomer in the final enantiomeric mixture would be that one which makes steric hindrance with the chiral photocatalyst and forms a disfavored catalytic cycle alongside a favored catalytic cycle which operates by the other enantiomer.

On the other hand, in photoredox catalysis, chiral organometallic complexes are mainly used, and the mechanism usually goes through different steps of single electron transfer (SET), hydrogen atom transfer (HAT) and enantioselective proton transfer (PT). It must be pointed out that in this mechanism each substrate can follow a specific and unique pathway based on its structural features. In some photoredox-based catalysis deracemization reactions, in addition to using the appropriate chiral photocatalyst, it may be necessary to use another additive.

Biosketches



Seyed Parsa Hashemian was born in 2003 in Karaj, Iran. He is currently a junior year B.Sc. student in chemistry at Kharazmi University, Tehran, Iran. In his early professional research, he focuses on photochemical deracemization reactions, a field he finds particularly interesting and intends to pursue further.



Tara Afshar Moghadam was born in 2002 in Tehran, Iran. At present, She is an undergraduate student of chemistry at Kharazmi University, Tehran, Iran. Her research interests encompass photochemical reactions and their pharmaceutical applications.



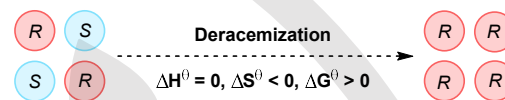
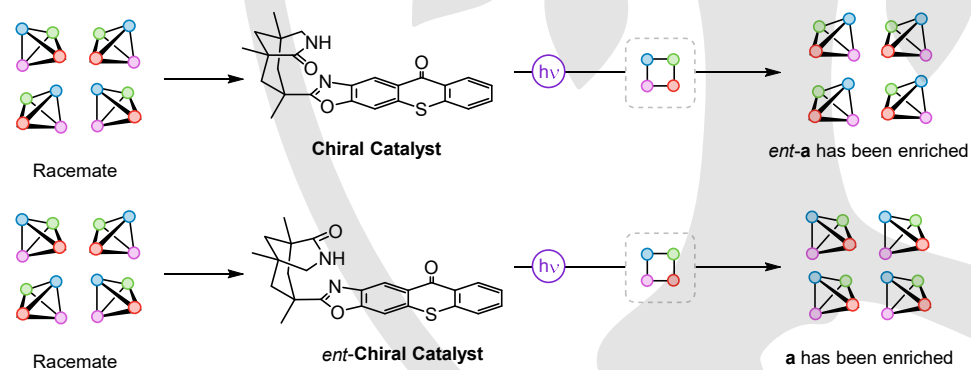
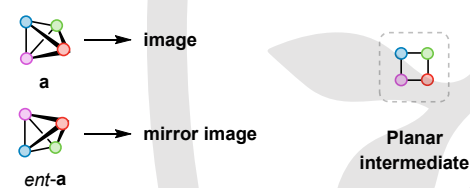
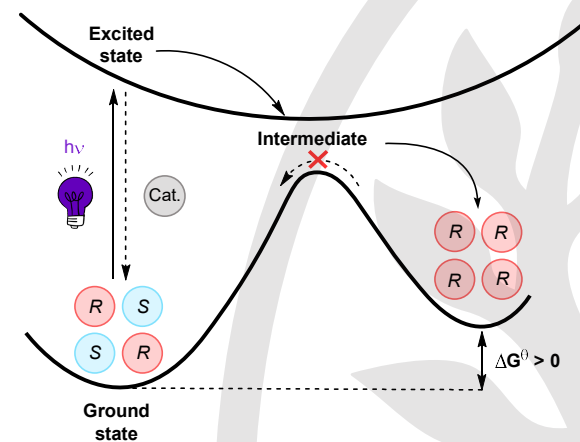
Seyed Mohammad Arabi Zanjani was born in 2002 in Tehran, Iran. Currently, he is an undergraduate student of chemistry at Kharazmi University, Tehran, Iran. In 2023, he joined the research group of Prof. Teimouri. His research interests include multi-component reactions and photochemical reactions.



Mohammad Bagher Teimouri (b. 1975) studied chemistry at Tabriz University, Iran, and completed his PhD in 2004 with Prof. Ahmad Shaabani at Shahid Beheshti University. After being Assistant Professor at Iran Polymer and Petrochemical Institute, he moved to Kharazmi University as an Associate Professor, where he was promoted to Full Professor in 2022. His research focuses on the development of new multicomponent reactions (MCRs), especially on isocyanide-based and enamione-based MCRs, MCRs in/on water, stereoselective transformations and synthesis of novel functional dyes.

Insert full-page Figures below: either (1) copy, paste, and replace the sample graphic box and caption, or (2) place the cursor at the beginning of the next line, then select 'Insert Figure' and 'Figure (for Graphical Review)' on the SynOpen ribbon tab.

A) EnT photocatalysis mechanism

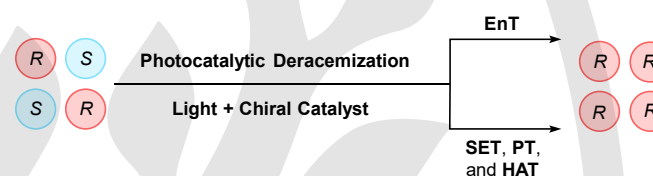


Challenges

- Thermodynamically disfavored
- Kinetic: microscopic reversibility

Requirements

- External sufficient energy input
- Distinct mechanistic pathways



Further Reading

- 1a) Huang, *J. Am. Chem. Soc.* **2023**, *145*, 10917.
- 1b) Yang, *Nature* **2018**, *564*, 197.
- 1c) Su, *Chin. J. Org. Chem.* **2022**, *42*, 3201.
- 1d) Blackmond, *Angew. Chem. Int. Ed.* **2009**, *48*, 2648.
- 1e) Wendlandt, *Science* **2019**, *366*, 304.

B) Photoredox catalysis mechanism

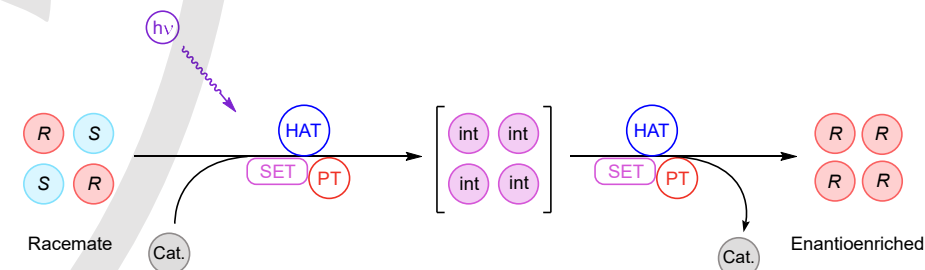
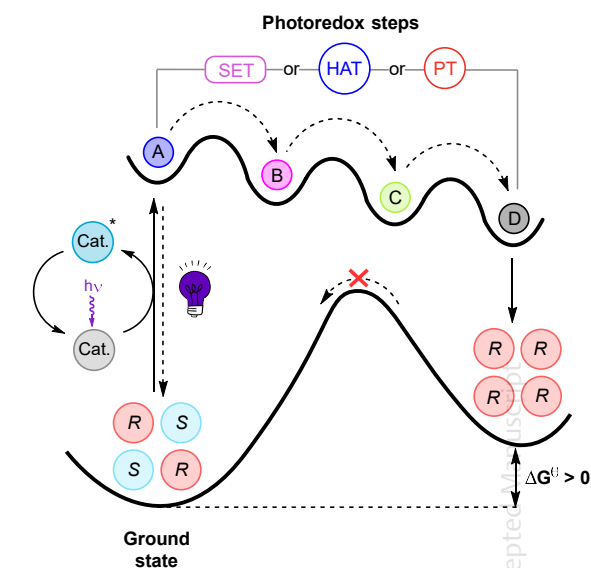
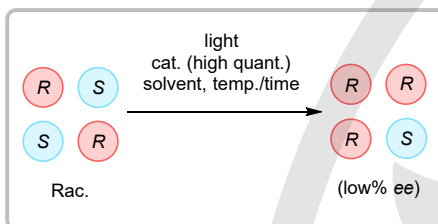


Figure 1 Overview of deracemization and distinct mechanisms for EnT catalytic and Photoredox catalysis deracemization reactions^{1a-e}

Primitive Reports on Light-Driven Deracemization Reactions



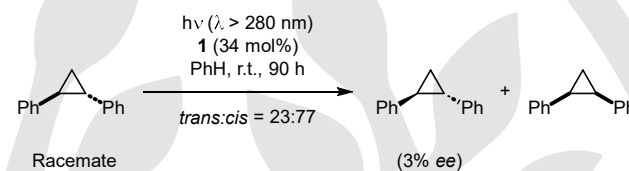
Notable Features

- Reactions proceed using simple chiral catalysts
- Utilization of a substantial quantity of catalysts to overcome thermodynamic and kinetic obstacles
- All reactions have been photochemically driven
- Low enantiomeric excess (*ee*)
- Demonstrating the reaction with diverse substrates highlights its applicability to various compounds

Further Reading

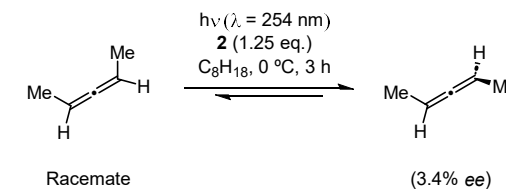
- 2a) Ouannès, *J. Am. Chem. Soc.* **1973**, 95, 8472.
 2b) Drucker, *J. Am. Chem. Soc.* **1973**, 95, 6482.
 2c) Balavoine, *Tetrahedron Lett.* **1973**, 14, 4159.
 2d) Tsuneishi, *J. Chem. Soc. Perkin Trans. 2*, **1996**, 1601.
 2e) Wang, *Chem. Eur. J.* **2023**, 29, e202204029.
 2f) Großkopf, *Chem. Rev.* **2022**, 122, 1626.

a) *trans*-1,2-Diphenylcyclopropane



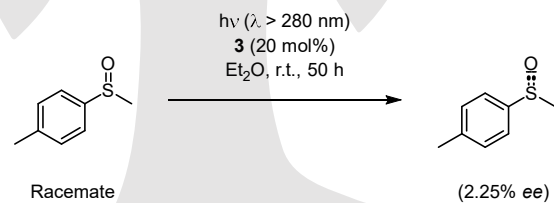
2a) Ouannès, *J. Am. Chem. Soc.* **1973**, 95, 8472.

b) 2,3-Pentadiene



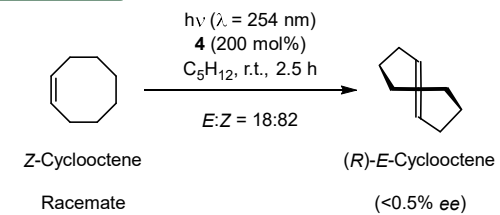
2b) Drucker, *J. Am. Chem. Soc.* **1973**, 95, 6482.

c) Sulfoxide



2c) Balavoine, *Tetrahedron Lett.* **1973**, 14, 4159.

d) Z-Cyclooctene



2d) Tsuneishi, *J. Chem. Soc. Perkin Trans. 2*, **1996**, 1601.

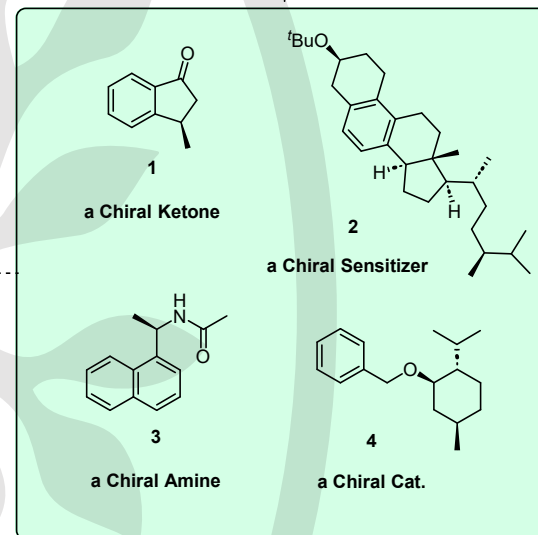
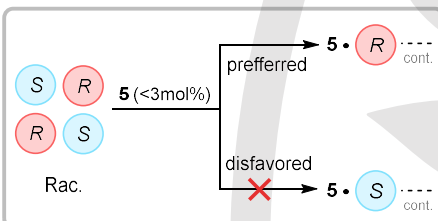
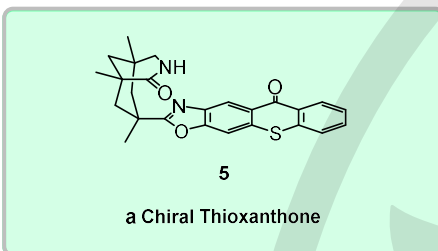


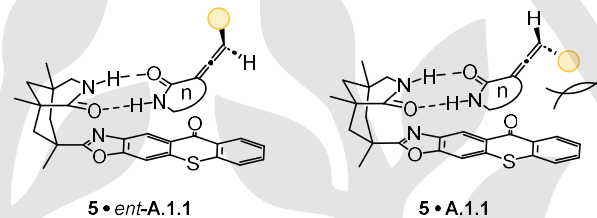
Figure 2 Primitive reports on photocatalytic deracemization reactions^{2a-f}

**A) Energy-Transfer-Based (EnT)
Photocatalytic Deracemization Reactions**

Notable Features

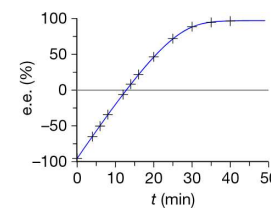
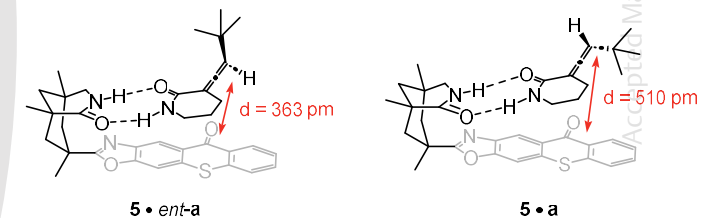
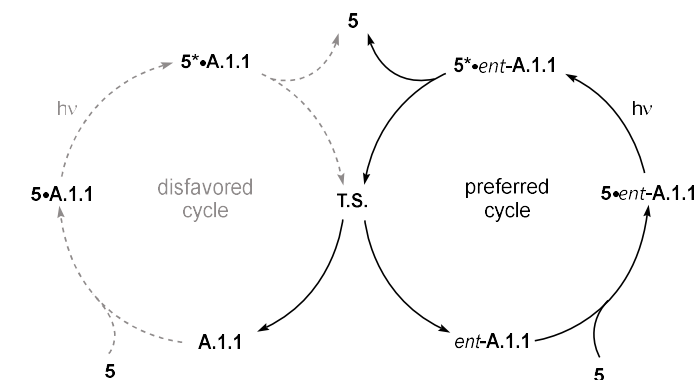
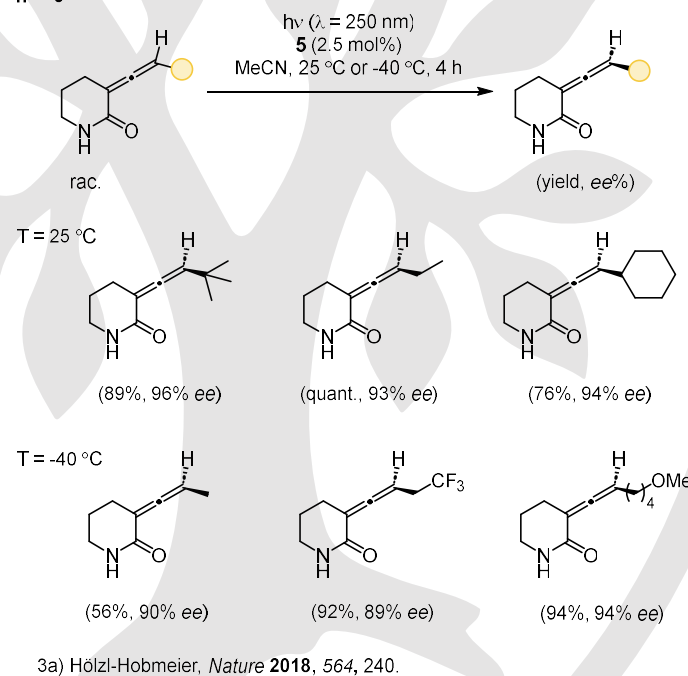
- Allene Lactams light-driven deracemization reactions proceed through a planar intermediate formed by C-C double bond cleavage
- The preferred cycle is always the one that avoids steric hindrance with catalyst **5**
- Always the enriched enantiomer is the one that doesn't prefer to form H-bonds with **5**

Further Reading

- 3a) Hölzl-Hobmeier, *Nature* **2018**, 564, 240.
 3b) Plaza, *Angew. Chem. Int. Ed.* **2020**, 59, 12785.
 3c) Großkopf, *Angew. Chem. Int. Ed.* **2023**, 62, e202308241.
 3d) Alonso, *Angew. Chem.* **2014**, 53, 4368.
 3e) Gotthardt, *Chem. Ber.* **1975**, 108, 657.
 3f) Shepard, *J. Am. Chem. Soc.* **1997**, 119, 2597.
 2e) Wang, *Chem. Eur. J.* **2023**, 29, e202204029.

A.1) Allenes
A.1.1) Allene Lactams


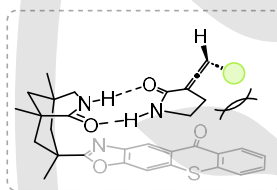
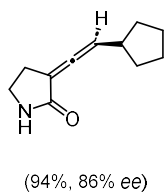
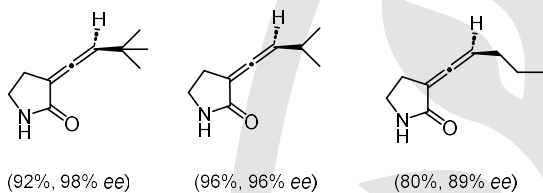
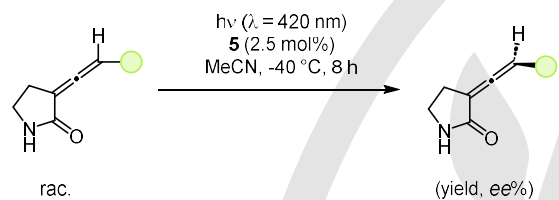
- 3a) Hölzl-Hobmeier, *Nature* **2018**, 564, 240.
 3b) Plaza, *Angew. Chem. Int. Ed.* **2020**, 59, 12785.

**Six-membered Allene Lactams
n = 6**


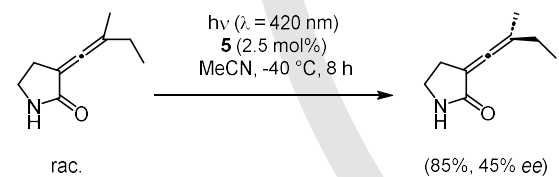
(ee% - time) graph of the conversion of ent-**a** to **a**, with Chiral Thioxanthone **5**.

- 3a) Hölzl-Hobmeier, *Nature* **2018**, 564, 240.
 3c) Großkopf, *Angew. Chem. Int. Ed.* **2023**, 62, e202308241.

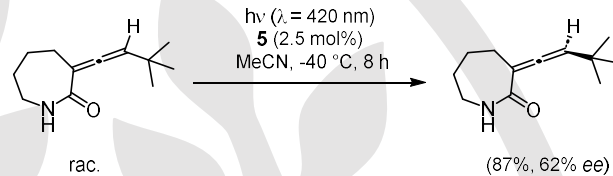
Figure 3 Light-driven deracemization reactions by Energy-Transfer-Based photocatalysis^{2e,3a-f}

Five-membered Allene Lactams
n = 5


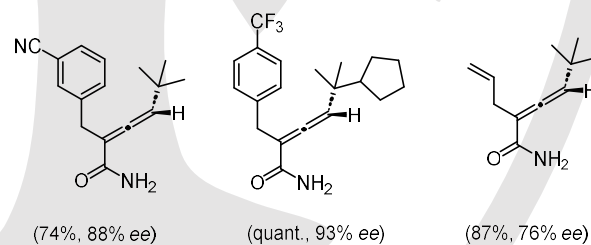
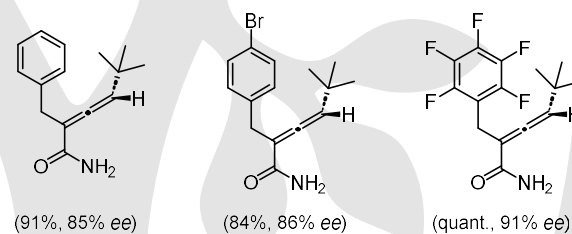
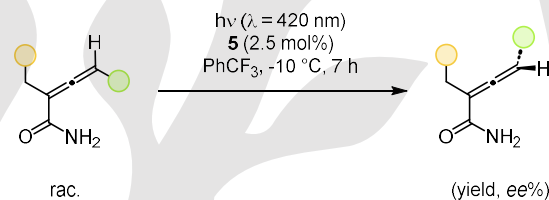
3b) Plaza, *Angew. Chem. Int. Ed.* **2020**, *59*, 12785.

Five-membered (dialkyl-substituted) Allene Lactams
n = 5


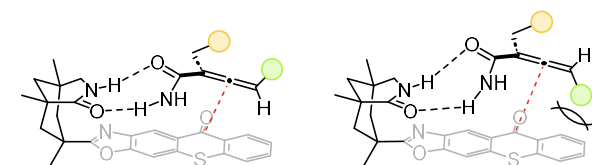
3b) Plaza, *Angew. Chem. Int. Ed.* **2020**, *59*, 12785.

Seven-membered Allene Lactams
n = 7


3b) Plaza, *Angew. Chem. Int. Ed.* **2020**, *59*, 12785.

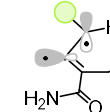
A.1.2) Allene Amides


4a) Plaza, *J. Am. Chem. Soc.* **2021**, *143*, 11209.



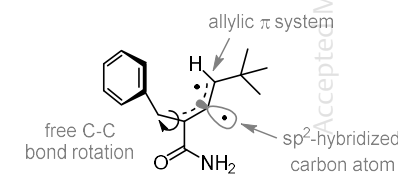
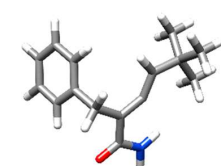
Faster Dexter-type energy transfer Slower Dexter-type energy transfer

2e) Wang, *Chem. Eur. J.* **2023**, *29*, e202204029.



Triplet State
(T.S.)

3c) Großkopf, *Angew. Chem. Int. Ed.* **2023**, *62*, e202308241.



DFT calculated structure

4a) Plaza, *J. Am. Chem. Soc.* **2021**, *143*, 11209.

Further Reading

- 4a) Plaza, *J. Am. Chem. Soc.* **2021**, *143*, 11209.
 4b) Burg, *J. Org. Chem.* **2019**, *84*, 8815.
 4c) Fackler, *J. Am. Chem. Soc.* **2012**, *134*, 12869.
 4d) Ye, *Org. Chem. Front.* **2014**, *1*, 1210.
 4e) Yu, *Angew. Chem. Int. Ed.* **2012**, *51*, 3074.
 3b) Plaza, *Angew. Chem. Int. Ed.* **2020**, *59*, 12785.
 3c) Großkopf, *Angew. Chem. Int. Ed.* **2023**, *62*, e202308241.
 2e) Wang, *Chem. Eur. J.* **2023**, *29*, e202204029.

Figure 4 Allene Lactams photochemical deracemization with presence of chiral Thioxanthone catalyst^{2e,3b,c,4a-e}

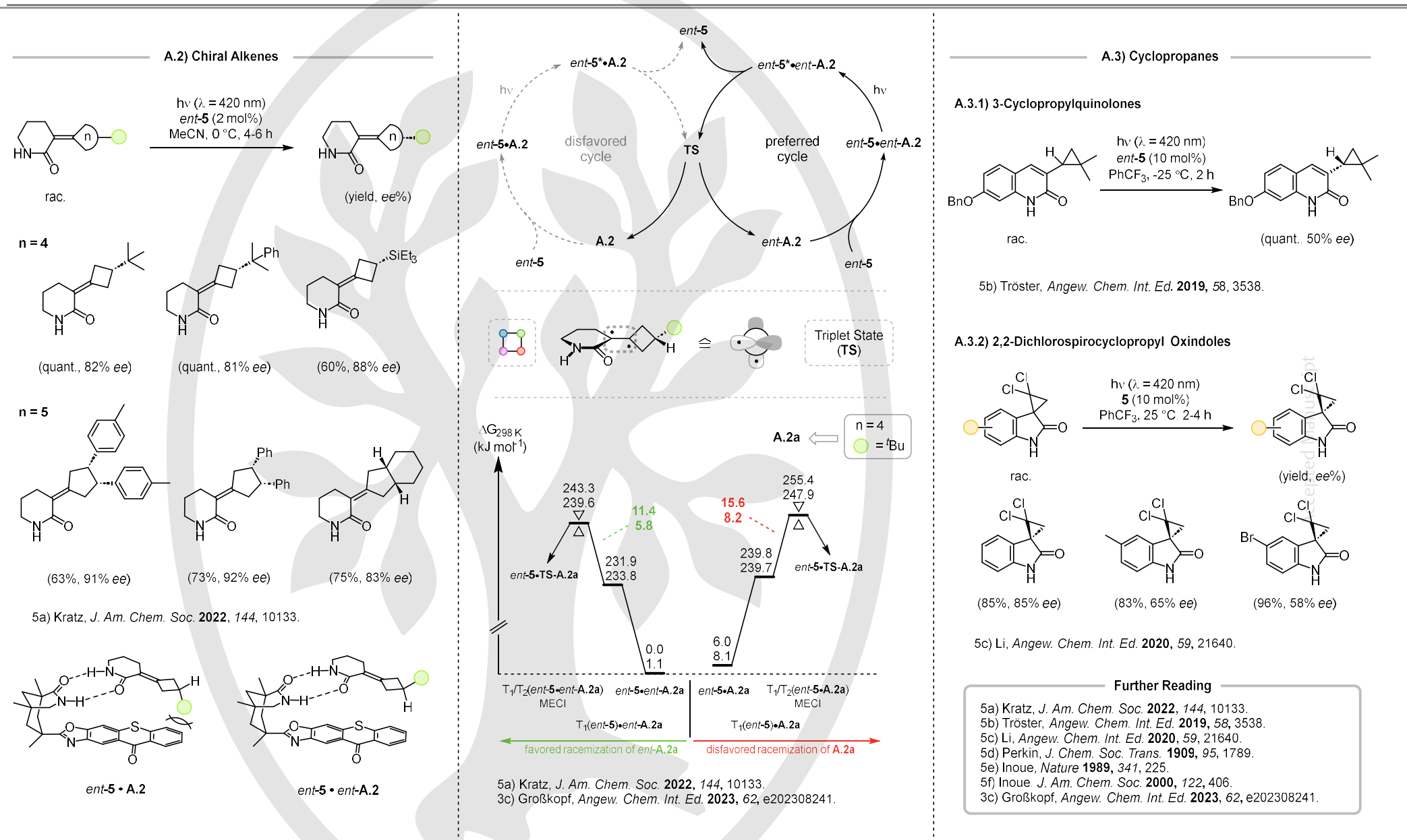


Figure 5 Mechanism and results of photochemical deracemization of Chiral Alkenes and Cyclopropanes^{3c,5a-f}

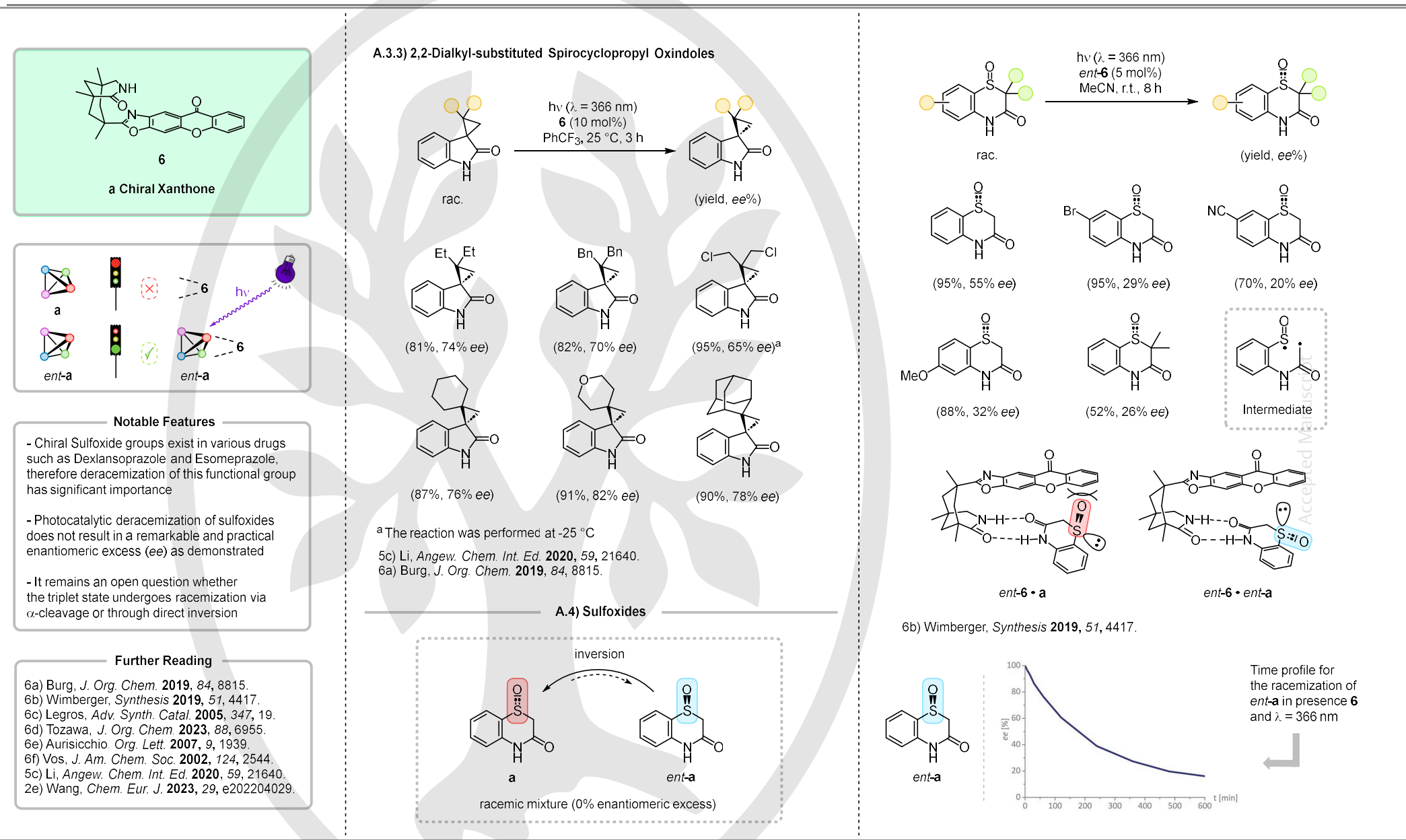


Figure 6 EnT based photocatalytic deracemization of Cyclopropanes and Sulfoxides using chiral Xanthone catalyst^{2e,5c,6a-f}

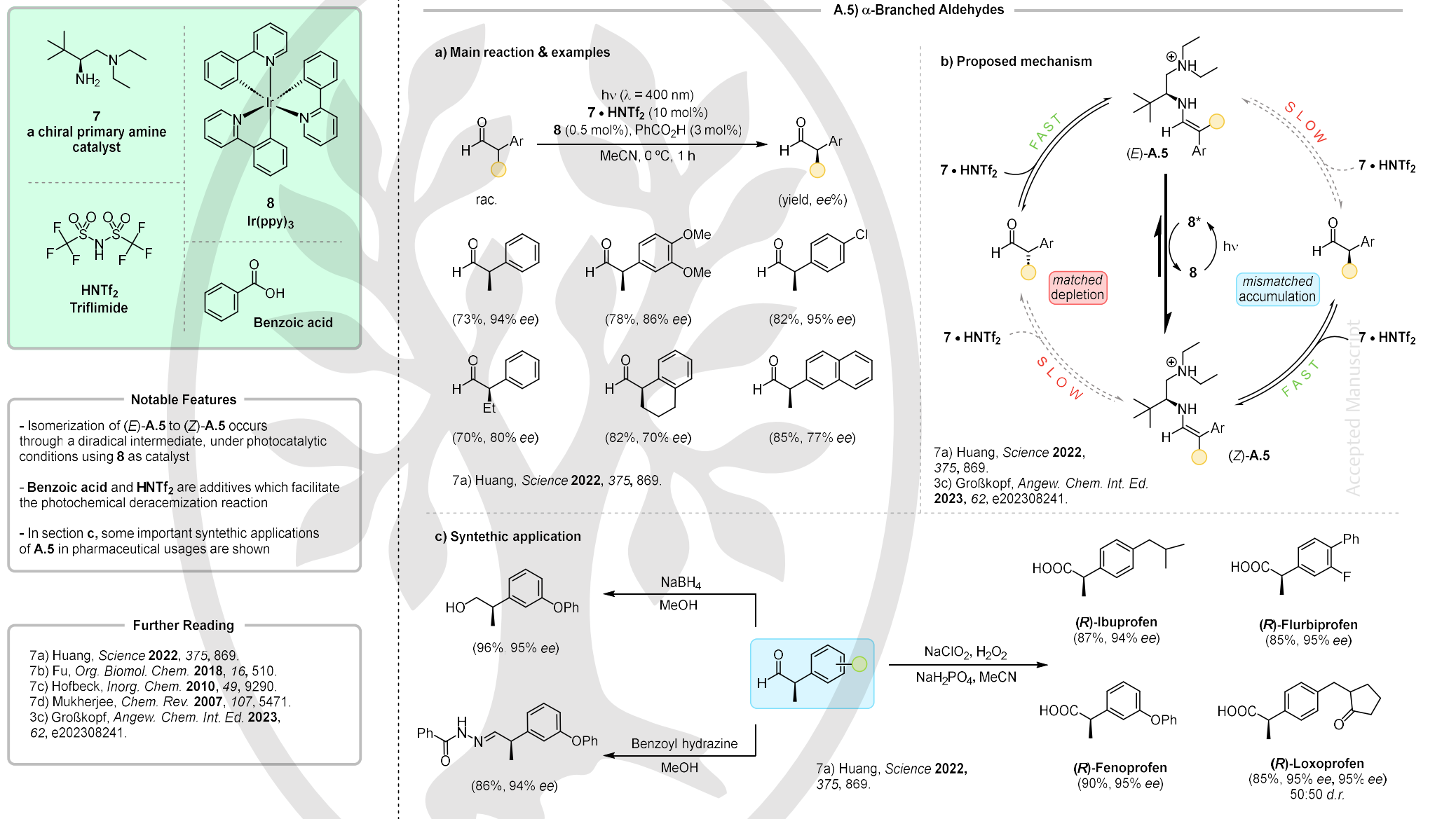
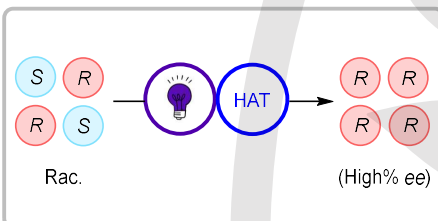
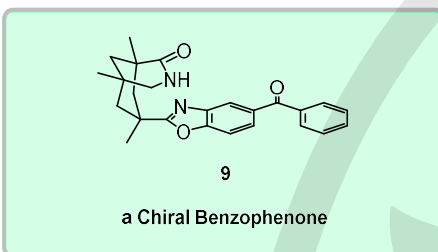


Figure 7 EnT based photocatalytic deracemization of α-Arylated Aldehydes using a chiral primary amine and a chiral Iridium complex as catalysts^{3c,7a-d}

B) Photocatalytic Deracemization Reactions By Photoredox Catalysis



Notable Features

- Photochemical deracemization using chiral benzophenone catalyst usually passes through two steps of HAT and one tautomerization step, respectively

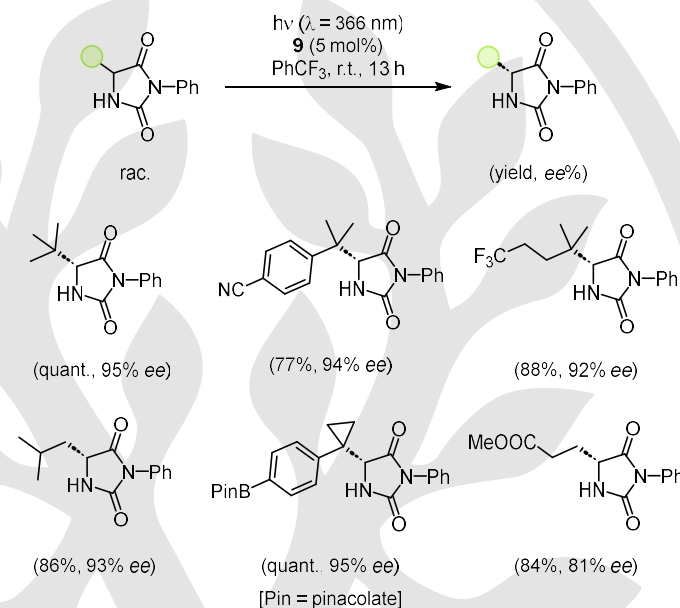
- It is crucial to know that the benzophenone catalyst exists as two enantiomers: **9**, which is the (+) enantiomer, and *ent*-**9**, the (-) enantiomer

- It is essential to consider that each enantiomer of the catalyst can result different enantioenrichment of a substrate

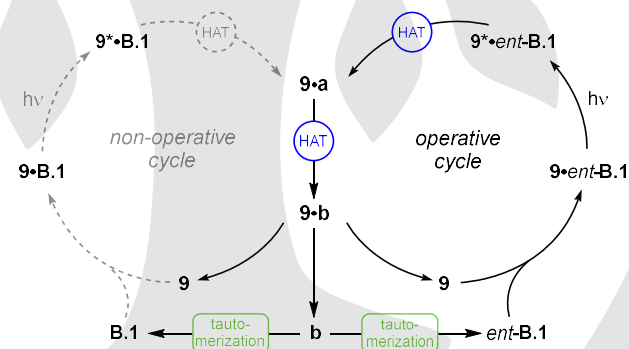
Further Reading

- 8a) Großkopf, *J. Am. Chem. Soc.* **2021**, *143*, 21241.
 8b) Kutta, *J. Am. Chem. Soc.* **2023**, *145*, 2354.
 8c) Großkopf, *Angew. Chem. Int. Ed.* **2023**, *62*, e202305274.
 3c) Großkopf, *Angew. Chem. Int. Ed.* **2023**, *62*, e202308241.

B.1) Hydantoins

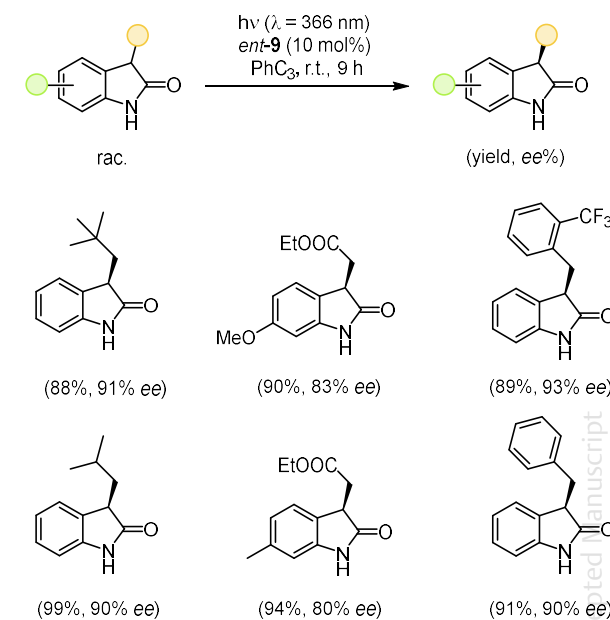


Proposed mechanism



- 8a) Großkopf, *J. Am. Chem. Soc.* **2021**, *143*, 21241.
 8b) Kutta, *J. Am. Chem. Soc.* **2023**, *145*, 2354.

B.2) 3-Substituted Oxindoles



8c) Großkopf, *Angew. Chem. Int. Ed.* **2023**, *62*, e202305274.

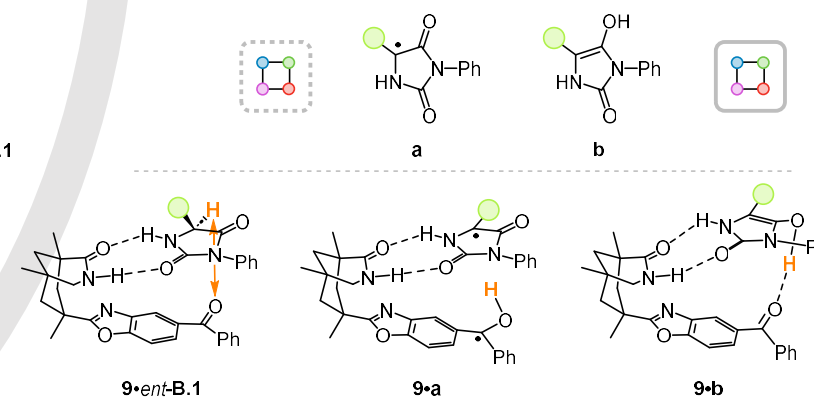


Figure 8 Photochemical deracemization reactions by photoredox catalysis with presence of a chiral Benzophenone^{3c,8a-c}

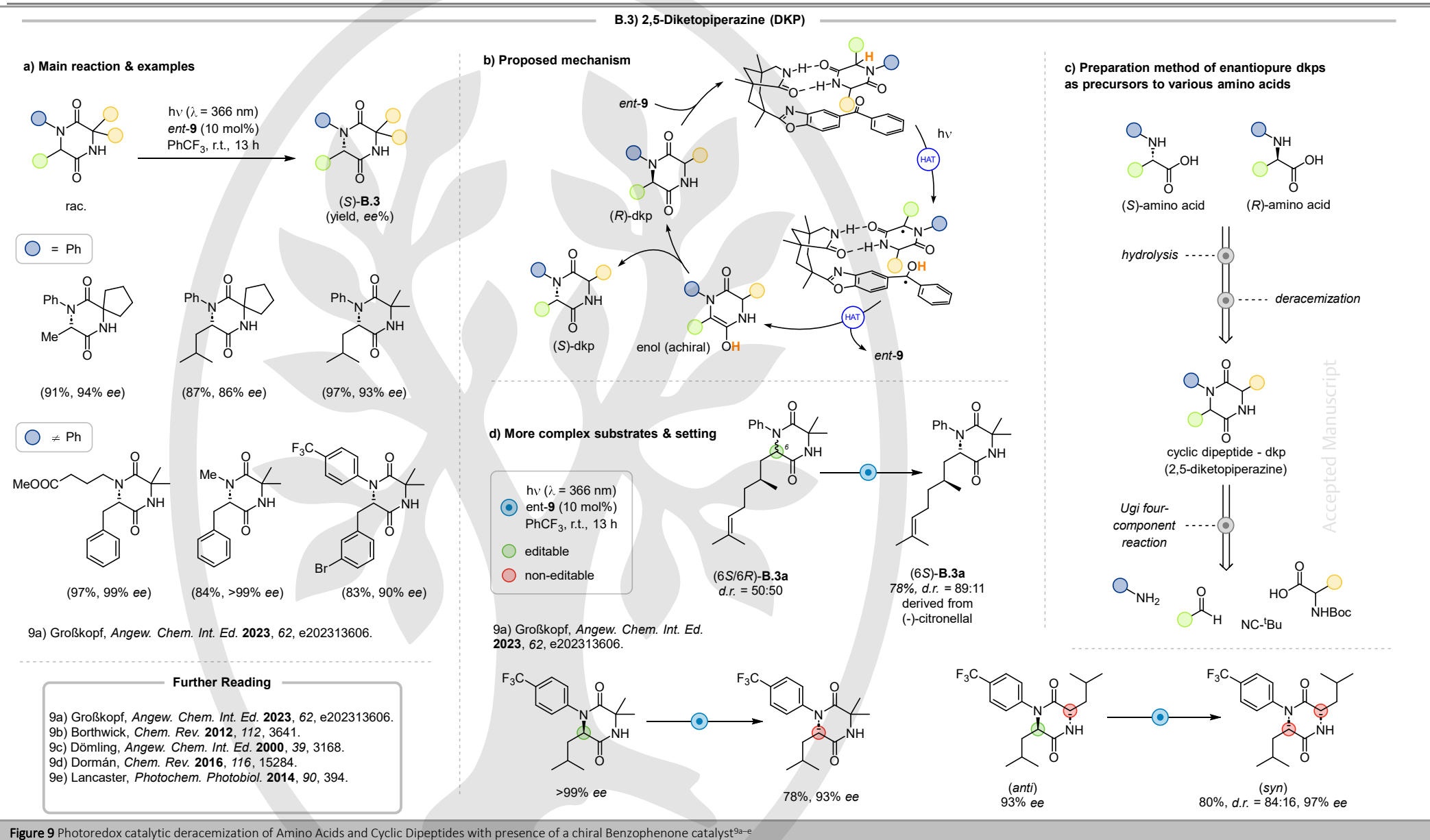


Figure 9 Photoredox catalytic deracemization of Amino Acids and Cyclic Dipeptides with presence of a chiral Benzophenone catalyst^{9a-e}

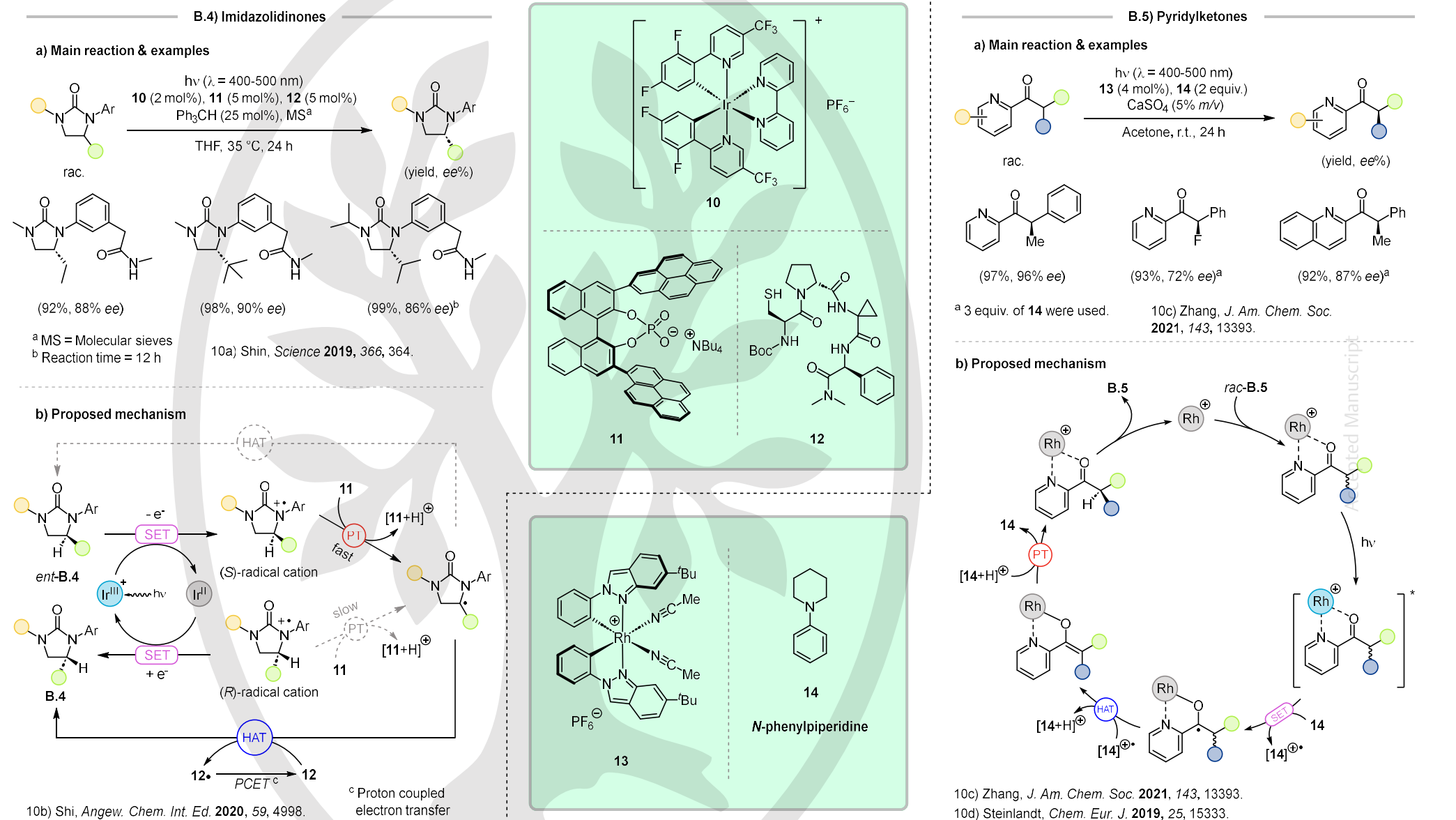


Figure 10 Deracemization of Imidazolidinones and Pyridylketones under photochemical conditions using chiral Iridium and Rhodium complexes, respectively^{10a-c}

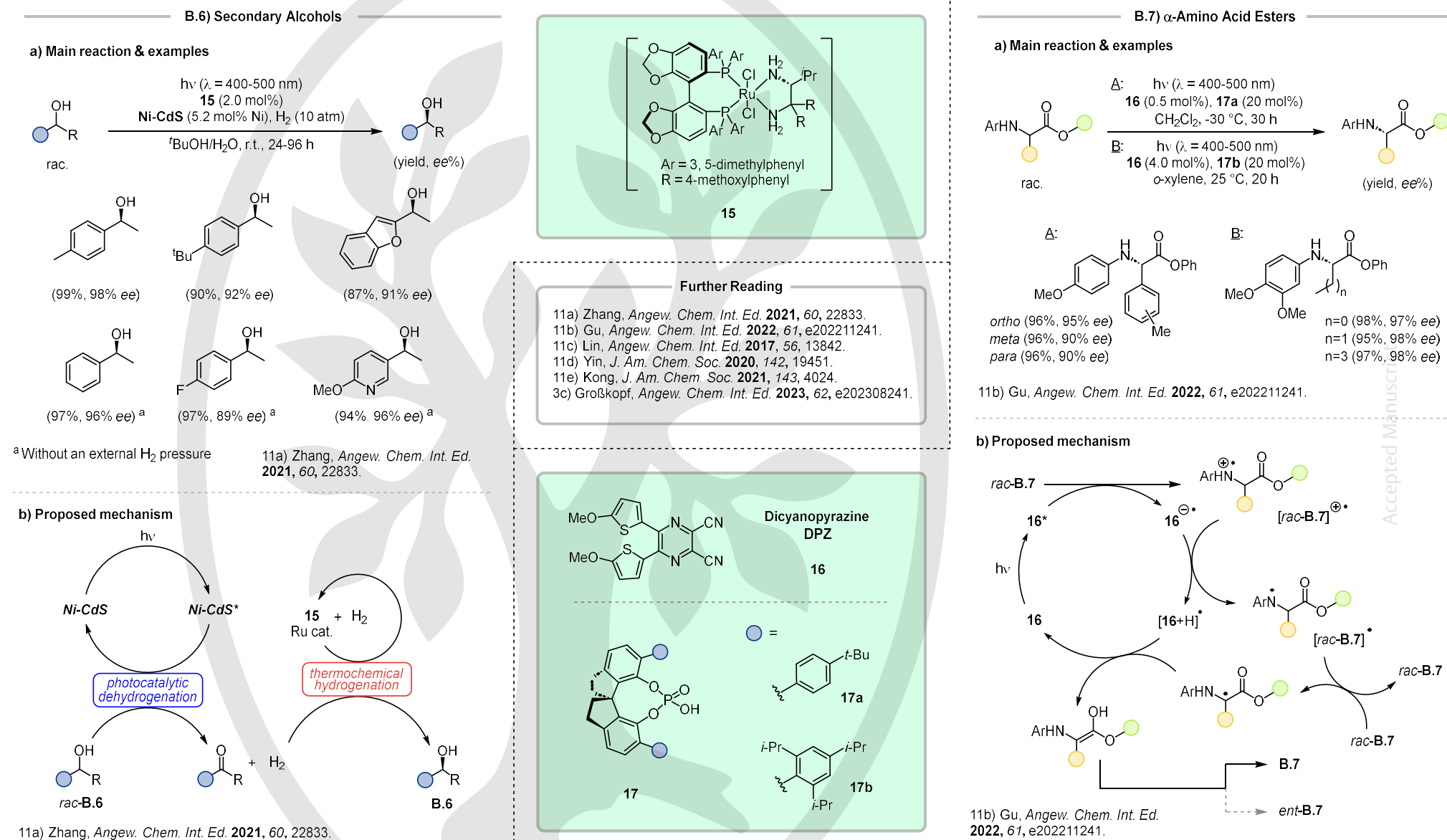


Figure 11 Photocatalytic deracemization reactions of Secondary Alcohols and α -Amino Acid Esters via photoredox catalysis mechanism^{3c,11a-e}

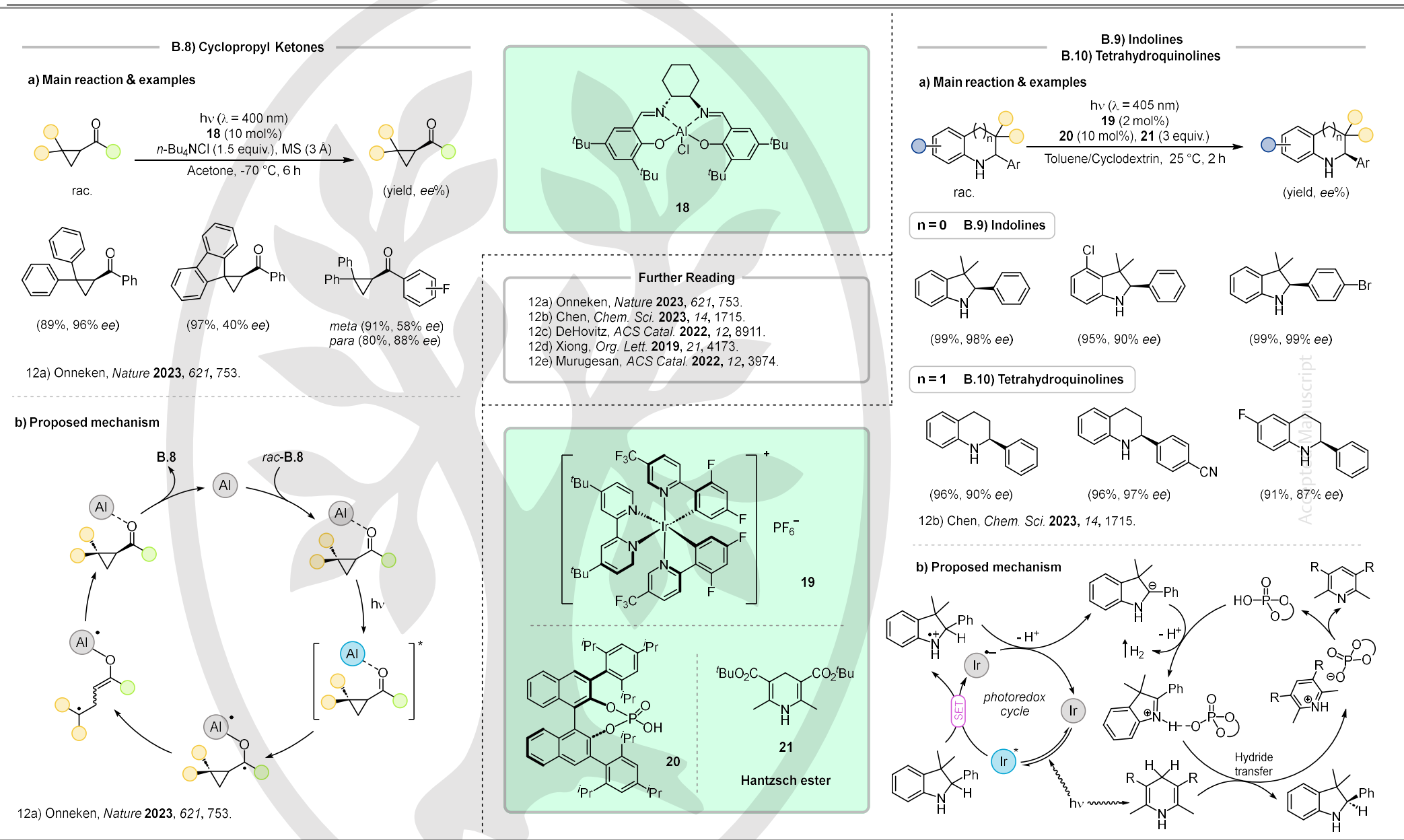


Figure 12 Photochemical deracemization of Cyclopropyl Ketones, Indolines and Tetrahydroquinolines via photoredox catalysis mechanism^{12a-e}

Insert all full-page Figures ahead of this line, and leave this line here – it includes a necessary section break.

Conflict of Interest

The authors declare no conflict of interest.

References

- (1) (a) Huang, M.; Pan, T.; Jiang, X.; Luo, S. *J. Am. Chem. Soc.* **2023**, *145*, 10917. (b) Yang, C.; Inoue, Y. *Nature* **2018**, *564*, 197. (c) Su, Y.; Zou, Y.; Xiao, W. *Chin. J. Org. Chem.* **2022**, *42*, 3201. (d) Blackmond, D. G. *Angew. Chem. Int. Ed.* **2009**, *48*, 2648. (e) Wendlandt, A. E. *Science* **2019**, *366*, 304.
- (2) (a) Ouaneš, C.; Beugelmans, R.; Roussi, G. *J. Am. Chem. Soc.* **1973**, *95*, 8472. (b) Drucker, C. S.; Toscano, V. G.; Weiss, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 6482. (c) Balavoine G.; Juge, S.; Kagan, H. B. *Tetrahedron Lett.* **1973**, *14*, 4159. (d) Tsuneishi, H.; Hakushi, T.; Inoue, Y. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1601. (e) Wang, J.; Lv, X.; Jiang, Z. *Chem. Eur. J.* **2023**, *29*, e202204029. (f) Großkopf, J.; Kratz, T.; Rigotti, T.; Bach, T. *Chem. Rev.* **2022**, *122*, 1626.
- (3) (a) Hölzl-Hobmeier, A.; Bauer, A.; Silva, A. V.; Huber, S. M.; Bannwarth, C.; Bach, T. *Nature* **2018**, *564*, 240. (b) Plaza, M.; Jandl, C.; Bach, T. *Angew. Chem. Int. Ed.* **2020**, *59*, 12785. (c) Großkopf, J.; Bach, T. *Angew. Chem. Int. Ed.* **2023**, *62*, e202308241. (d) Alonso, R.; Bach, T. *Angew. Chem.* **2014**, *53*, 4368. (e) Gotthardt, H.; Hammond, G. S. *Chem. Ber.* **1975**, *108*, 657. (f) Shepard, M. S.; Carreira, E. M. *J. Am. Chem. Soc.* **1997**, *119*, 2597.
- (4) (a) Plaza, M.; Großkopf, J.; Breitenlechner, S.; Bannwarth, C.; Bach, T. *J. Am. Chem. Soc.* **2021**, *143*, 11209. (b) Burg, F.; Bach, T. *J. Org. Chem.* **2019**, *84*, 8815. (c) Fackler, P.; Huber, S. M.; Bach, T. *J. Am. Chem. Soc.* **2012**, *134*, 12869. (d) Ye, J.; Ma, S. *Org. Chem. Front.* **2014**, *1*, 1210. (e) Yu, S.; Ma, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 3074.
- (5) (a) Kratz, T.; Steinbach, P.; Breitenlechner, S.; Storch, G.; Bannwarth, C.; Bach, T. *J. Am. Chem. Soc.* **2022**, *144*, 10133. (b) Tröster, A.; Bauer, A.; Jandl, C.; Bach, T. *Angew. Chem. Int. Ed.* **2019**, *58*, 3538. (c) Li, X.; Kutta, R. J.; Jandl, C.; Bauer, A.; Nuernberger, P.; Bach, T. *Angew. Chem. Int. Ed.* **2020**, *59*, 21640. (d) Perkin, W. H.; Pope, W. J.; Wallach, O. *J. Chem. Soc. Trans.* **1909**, *95*, 1789. (e) Inoue, Y.; Yokoyama, T.; Yamasaki, N.; Tai, A. *Nature* **1989**, *341*, 225. (f) Inoue, Y.; Ikeda, H.; Kaneda, M.; Sumimura, T.; Everitt, S. R. L.; Wada, T. *J. Am. Chem. Soc.* **2000**, *122*, 406.
- (6) (a) Burg, F.; Bach, T. *J. Org. Chem.* **2019**, *84*, 8815. (b) Wimberger, L.; Kratz, T.; Bach, T. *Synthesis* **2019**, *51*, 4417. (c) Legros, J.; Dehli, J. R.; Bolm, C. *Adv. Synth. Catal.* **2005**, *347*, 19. (d) Tozawa, K.; Makino, K.; Tanaka, Y.; Nakamura, K.; Inagaki, A.; Tabata, H.; Oshitari, T.; Natsugari, H.; Kuroda, N.; Kanemaru, K.; Oda, Y.; Takahashi, H. *J. Org. Chem.* **2023**, *88*, 6955. (e) Aurisicchio, C.; Baciocchi, E.; Gerini, M. F.; Lanzalunga, O. *Org. Lett.* **2007**, *9*, 1939. (f) Vos, B. W.; Jenks, W. S. *J. Am. Chem. Soc.* **2002**, *124*, 2544.
- (7) (a) Huang, M.; Zhang, L.; Pan, T.; Luo, S. *Science* **2022**, *375*, 869. (b) Fu, N.; Zhang, L.; Luo, S. *Org. Biomol. Chem.* **2018**, *16*, 510. (c) Hofbeck, T.; Yersin, H. *Inorg. Chem.* **2010**, *49*, 9290. (d) Mukherjee, S.; Yang, J. W.; Hoffmann, S.; List, B. *Chem. Rev.* **2007**, *107*, 5471.
- (8) (a) Großkopf, J.; Plaza, M.; Seitz, A.; Breitenlechner, S.; Storch, G.; Bach, T. *J. Am. Chem. Soc.* **2021**, *143*, 21241. (b) Kutta, R. J.; Großkopf, J.; van Staalduinen, N.; Seitz, A.; Pracht, P.; Breitenlechner, S.; Bannwarth, C.; Nuernberger, P.; Bach, T. *J. Am. Chem. Soc.* **2023**, *145*, 2354. (c) Großkopf, J.; Heidecker, A. A.; Bach, T. *Angew. Chem. Int. Ed.* **2023**, *62*, e202305274.
- (9) (a) Großkopf, J.; Plaza, M.; Kutta, R. J.; Nuernberger, P.; Bach, T. *Angew. Chem. Int. Ed.* **2023**, *62*, e202313606. (b) Borthwick, A. D. *Chem. Rev.* **2012**, *112*, 3641. (c) Dömling, A.; Ugi, I. *Angew. Chem. Int. Ed.* **2000**, *39*, 3168. (d) Dormán, G.; Nakamura, H.; Pulsipher, A.; Prestwich, G. D. *Chem. Rev.* **2016**, *116*, 15284. (e) Lancaster, J. R.; Smilowitz, R.; Turro, N. J.; Koberstein, J. T. *Photochem. Photobiol.* **2014**, *90*, 394.
- (10) (a) Shin, N. Y.; Ryss, J. M.; Zhang, X.; Miller, S. J.; Knowles, R. R. *Science* **2019**, *366*, 364. (b) Shi, Q.; Ye, J. *Angew. Chem. Int. Ed.* **2020**, *59*, 4998. (c) Zhang, C.; Gao, A. Z.; Nie, X.; Ye, C.-X.; Ivlev, S. I.; Chen, S.; Meggers, E. *J. Am. Chem. Soc.* **2021**, *143*, 13393. (d) Steinlandt, P. S.; Zuo, W.; Harms, K.; Meggers, E. *Chem. Eur. J.* **2019**, *25*, 15333.
- (11) (a) Zhang, Z.; Hu, X. *Angew. Chem. Int. Ed.* **2021**, *60*, 22833. (b) Gu, Z.; Zhang, L.; Li, H.; Cao, S.; Yin, Y.; Zhao, X.; Ban, X.; Jiang, Z. *Angew. Chem. Int. Ed.* **2022**, *61*, e202211241. (c) Lin, L.; Bai, X.; Ye, X.; Zhao, X.; Tan, C.-H.; Jiang, Z. *Angew. Chem. Int. Ed.* **2017**, *56*, 13842. (d) Yin, Y.; Li, Y.; Gonçalves, T. P.; Zhan, Q.; Wang, G.; Zhao, X.; Qiao, B.; Huang, K.-W.; Jiang, Z. *J. Am. Chem. Soc.* **2020**, *142*, 19451. (e) Kong, M.; Tan, Y.; Zhao, X.; Qiao, B.; Tan, C.-H.; Cao, S.; Jiang, Z. *J. Am. Chem. Soc.* **2021**, *143*, 4024.
- (12) (a) Onneken, C.; Morack, T.; Sokolova, O.; Niemeyer, N.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Neugebauer, J.; Gilmour, R. *Nature* **2023**, *621*, 753. (b) Chen, Q.; Zhu, Y.; Shi, X.; Huang, R.; Jiang, C.; Zhang, K.; Liu, G. *Chem. Sci.* **2023**, *14*, 1715. (c) DeHovitz, J. S.; Hyster, T. K. *ACS Catal.* **2022**, *12*, 8911. (d) Xiong, W.; Li, S.; Fu, B.; Wang, J.; Wang, Q.; Yang, W. *Org. Lett.* **2019**, *21*, 4173. (e) Murugesan, K.; Donabauer, K.; Narobe, R.; Derdau, V.; Bauer, A.; König, B. *ACS Catal.* **2022**, *12*, 3974.