



光催化的高效去消旋化反应

汇报人：黄言恺

指导老师：麻生明 教授

汇报日期：2023.9.22

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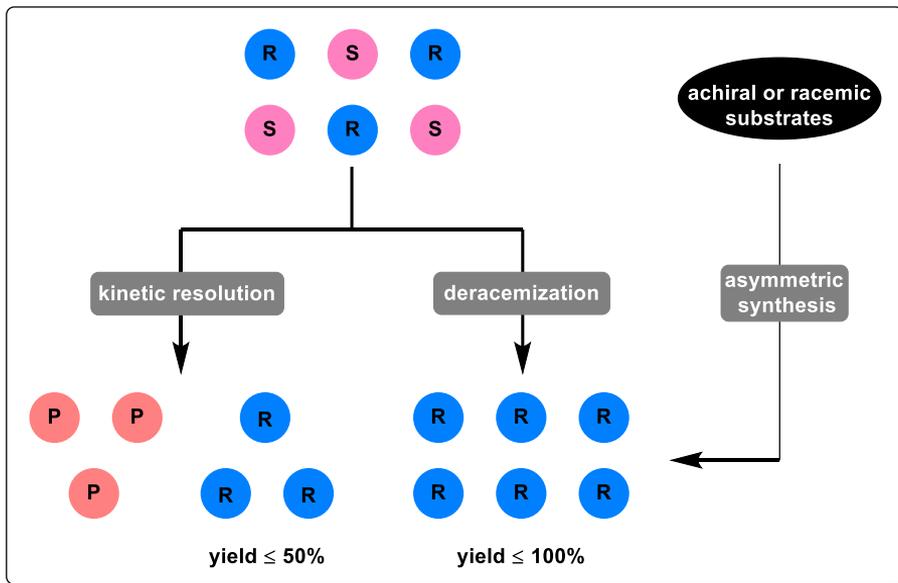
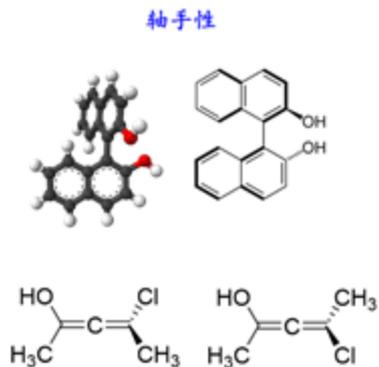
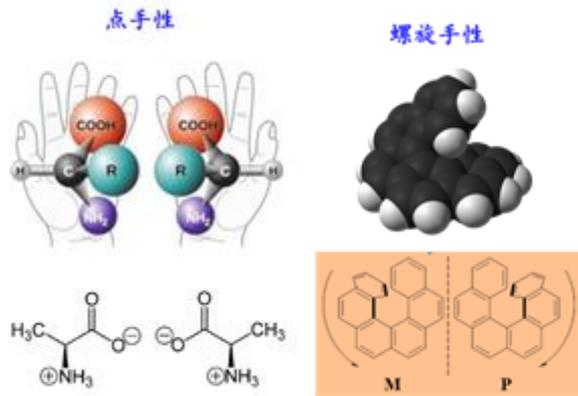
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- 2/ EnT过程去消旋化
- 3/ SET过程去消旋化
- 4/ HAT过程去消旋化
- 5/ 总结与展望

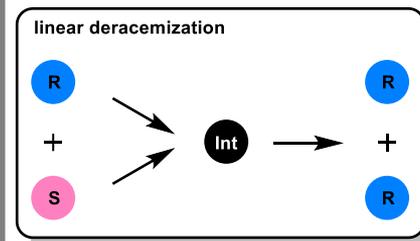
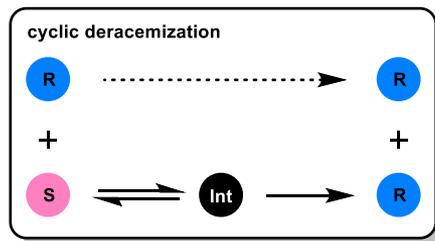
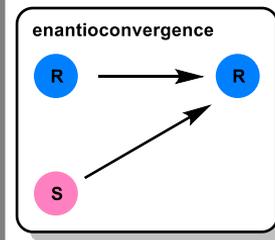
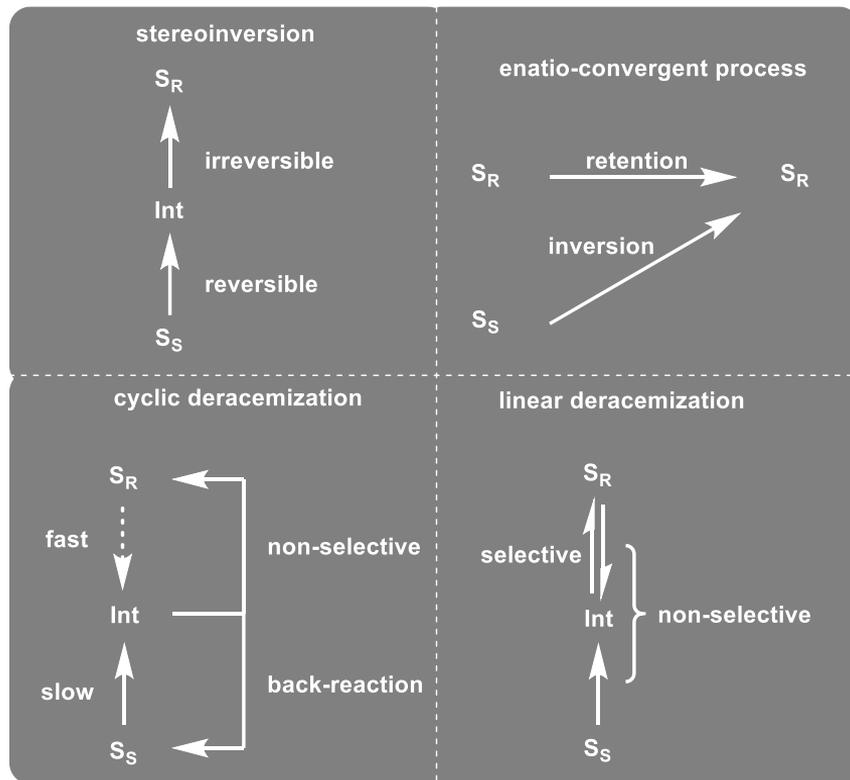
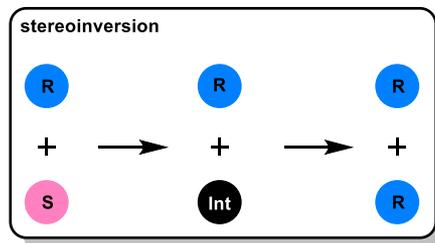
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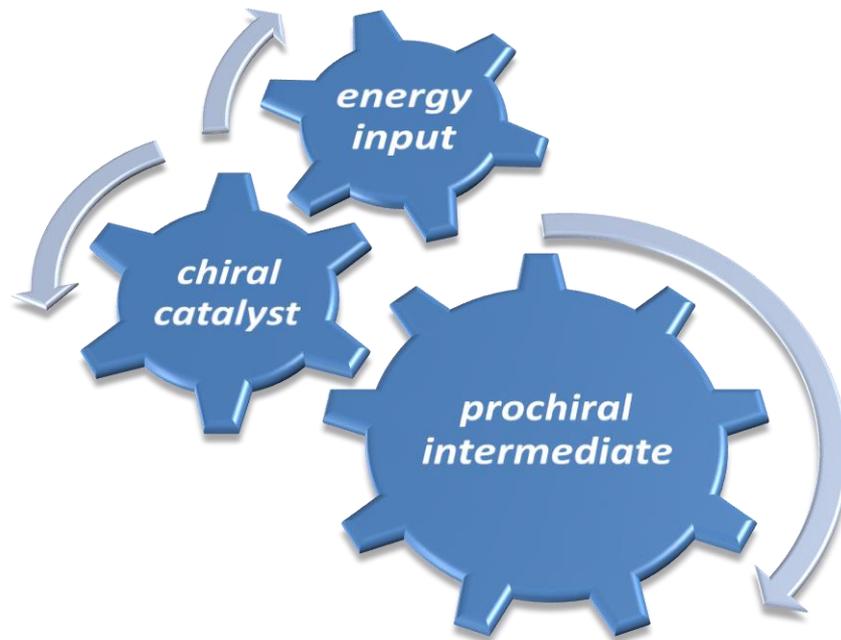
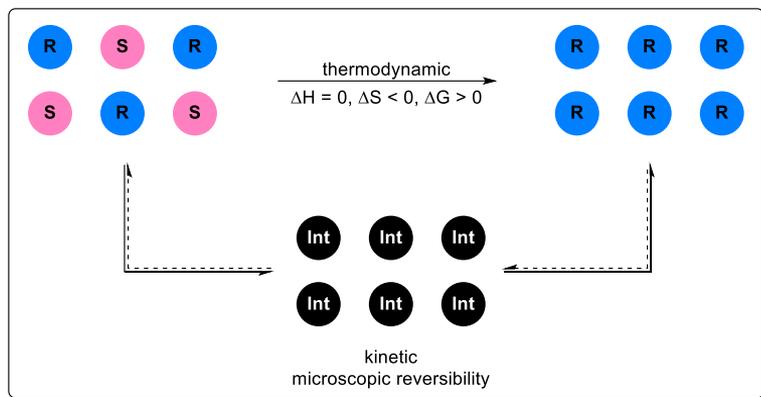
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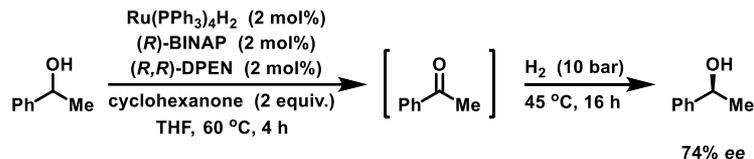
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研究背景

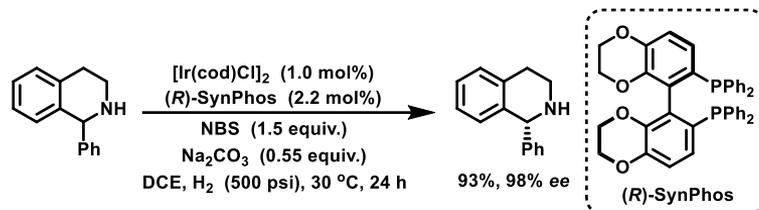




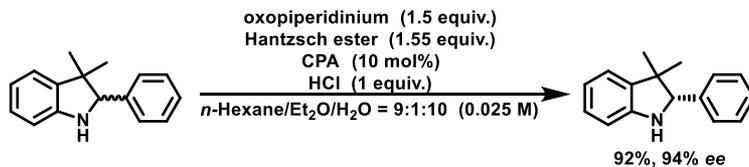




M. J. Williams Group
Chem. Commun.
2005, 5578-5579



Y. G. Zhou Group
J. Am. Chem. Soc.
2015, 137, 10496-10499



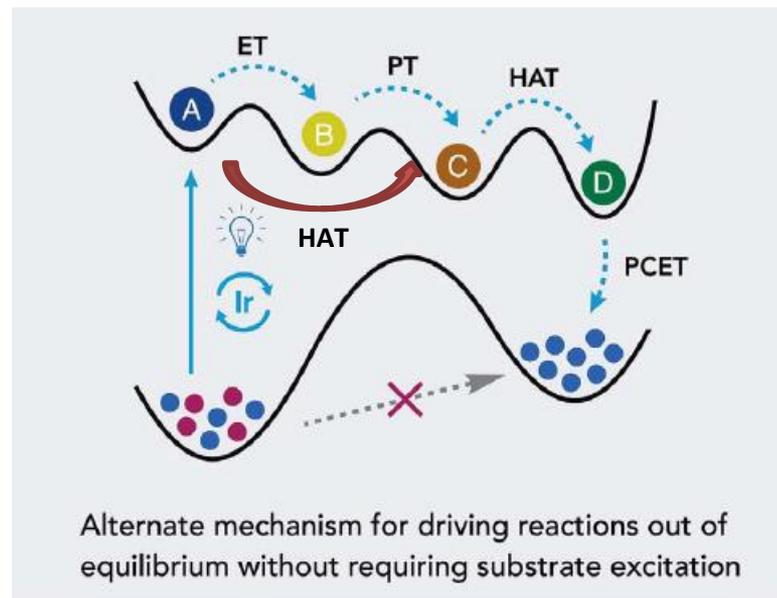
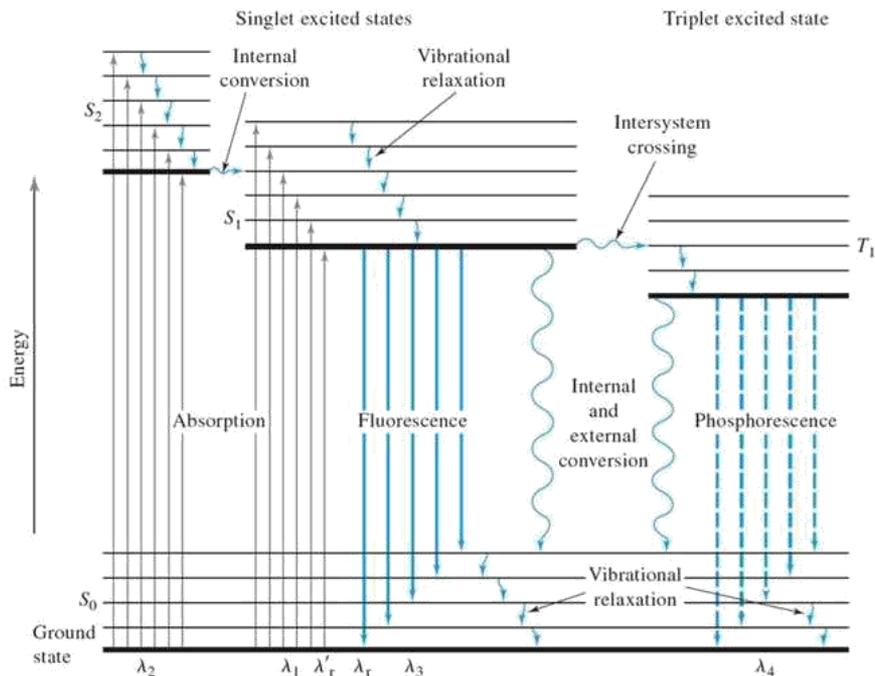
F. D. Toste Group
J. Am. Chem. Soc.
2013, 135, 14090-14093



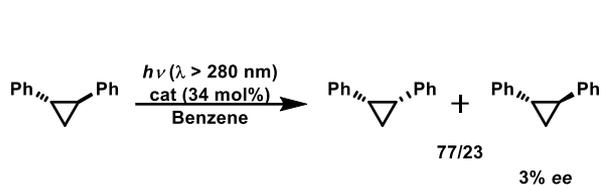
L. Liu Group
Angew. Chem. Int. Ed.
2017, 56, 5116-5120

Fluorescence Spectroscopy

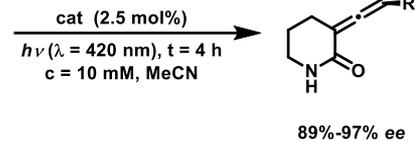
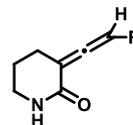
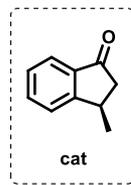
Jablonski Energy Diagram



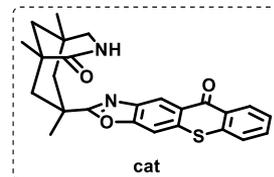
Alternate mechanism for driving reactions out of equilibrium without requiring substrate excitation



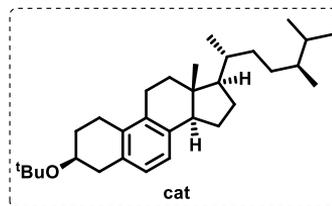
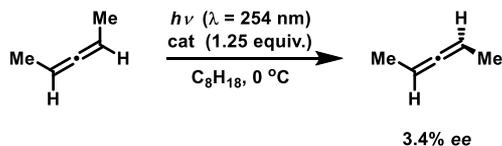
G. Roussi Group
J. Am. Chem. Soc.
 1973, 95, 8472-8474



T. Bach Group
Nature
 2018, 564, 240-243



R. G. Weiss Group
J. Am. Chem. Soc.
 1973, 95, 6482-6484

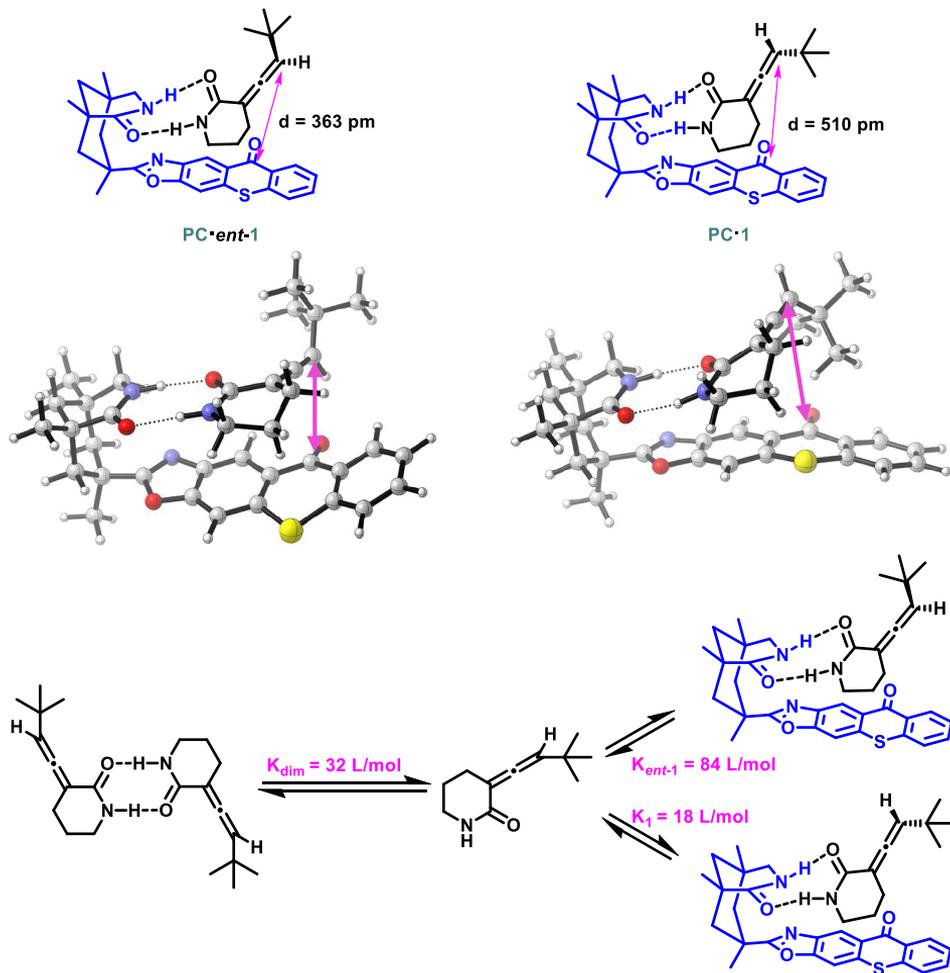
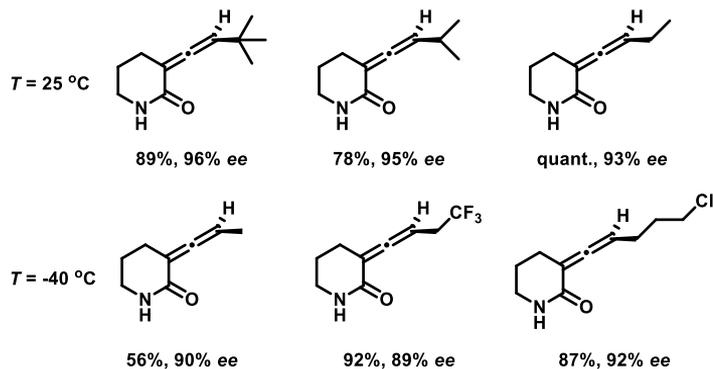
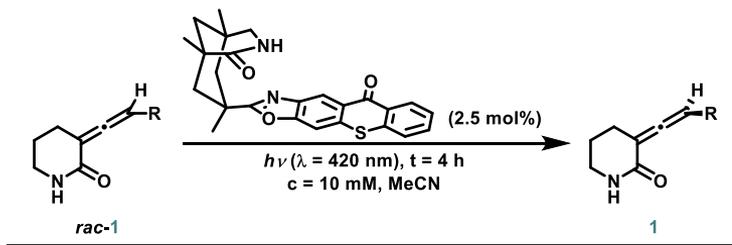


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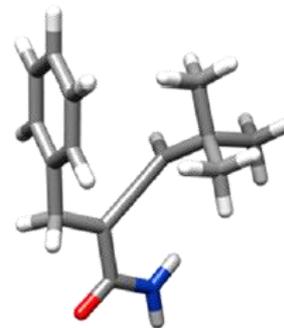
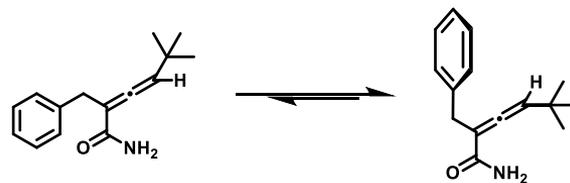
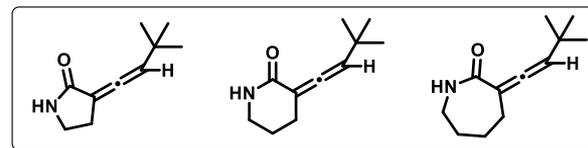
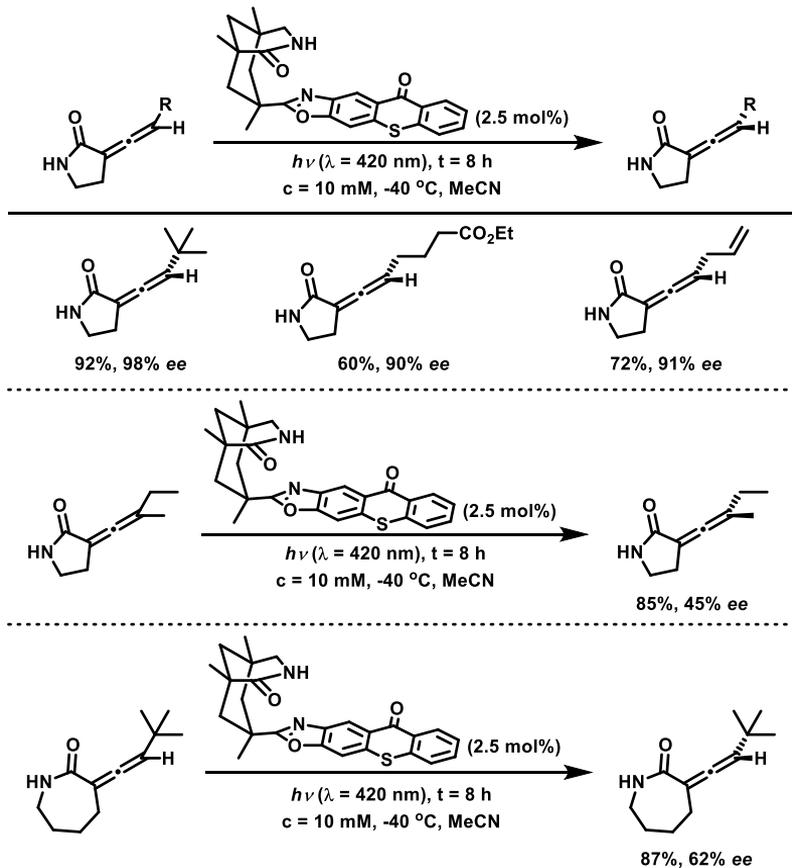
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EnT过程去消旋化



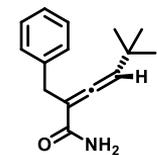
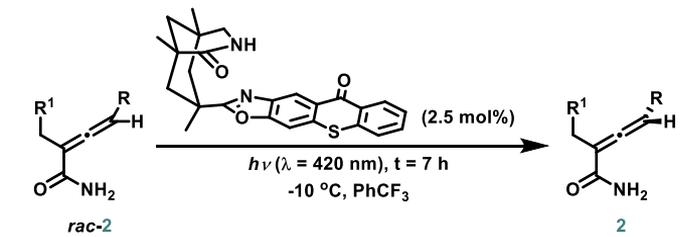
EnT过程去消旋化



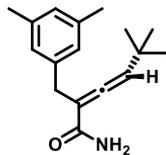
T. Bach *et al.*, *Angew. Chem. Int. Ed.* **2020**, *59*, 12785-12788

T. Bach *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 11209-11217

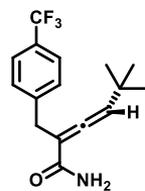
EnT过程去消旋化



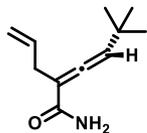
91%, 85% ee



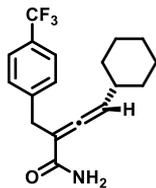
quant., 93% ee



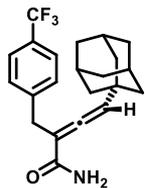
89%, 90% ee



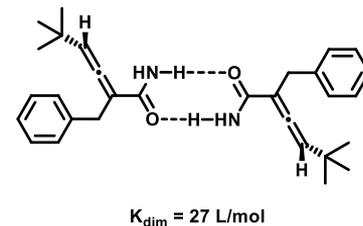
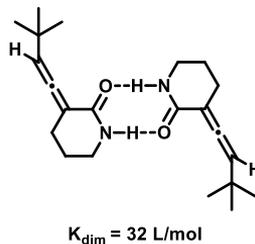
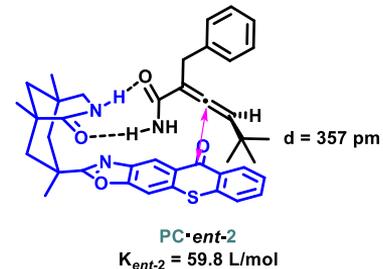
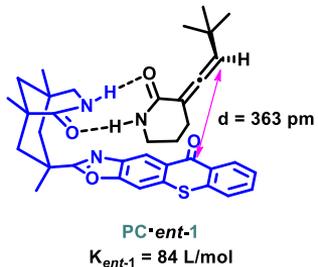
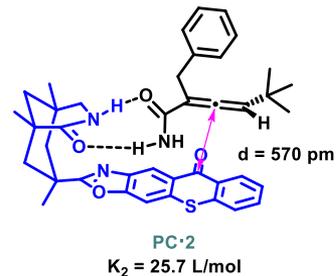
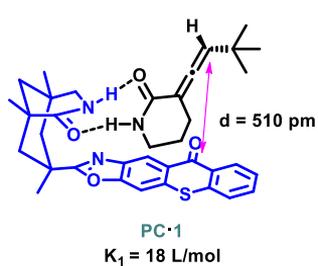
87%, 76% ee



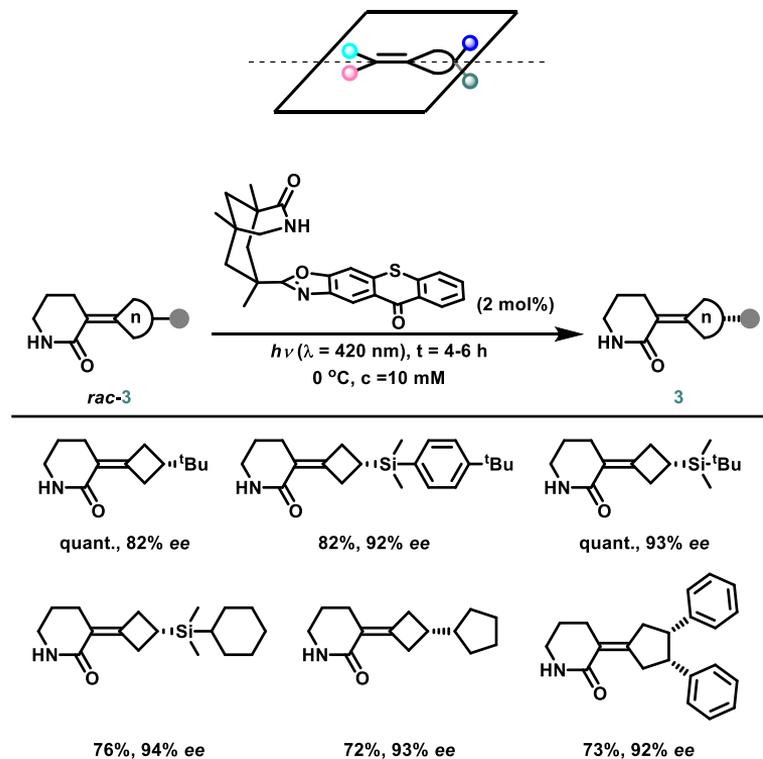
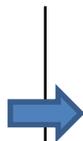
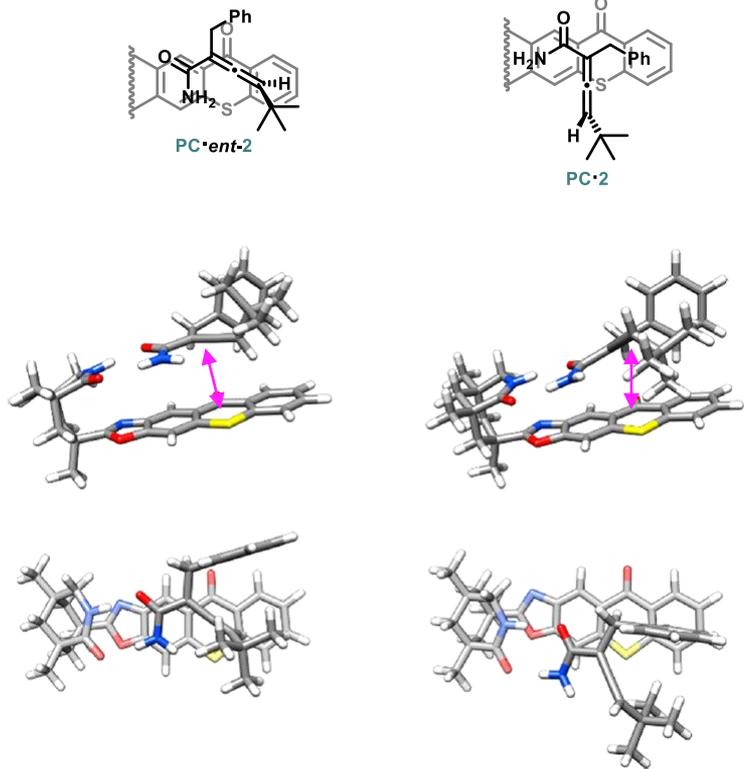
quant., 70% ee



83%, 72% ee

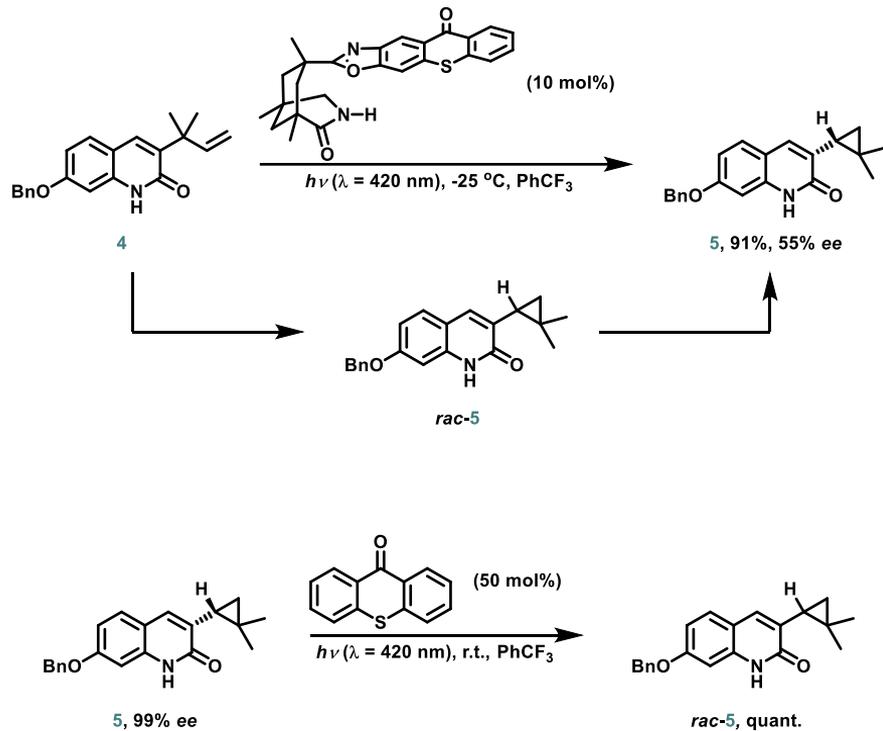


EnT过程去消旋化

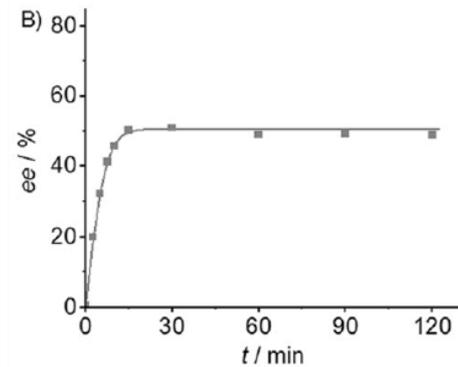
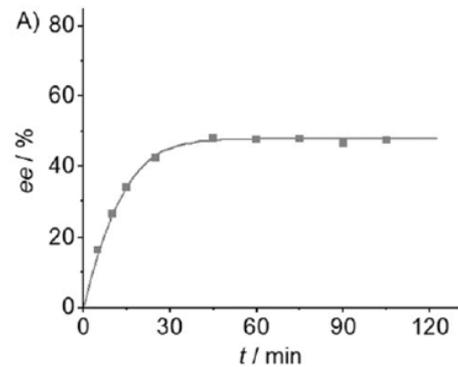


T. Bach *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 11209-11217

T. Bach *et al.*, *J. Am. Chem. Soc.* **2022**, *144*, 10133-10138

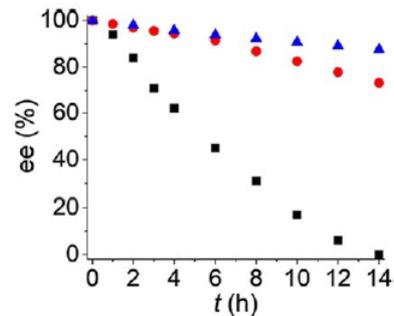
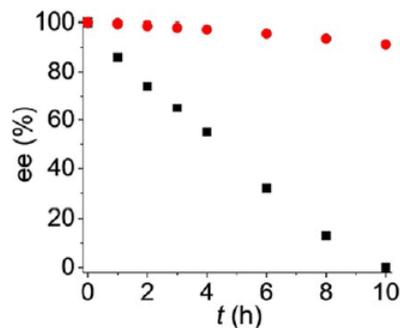
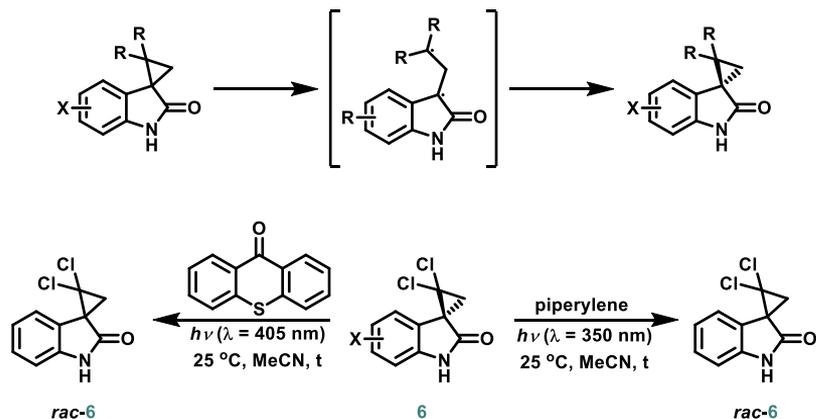
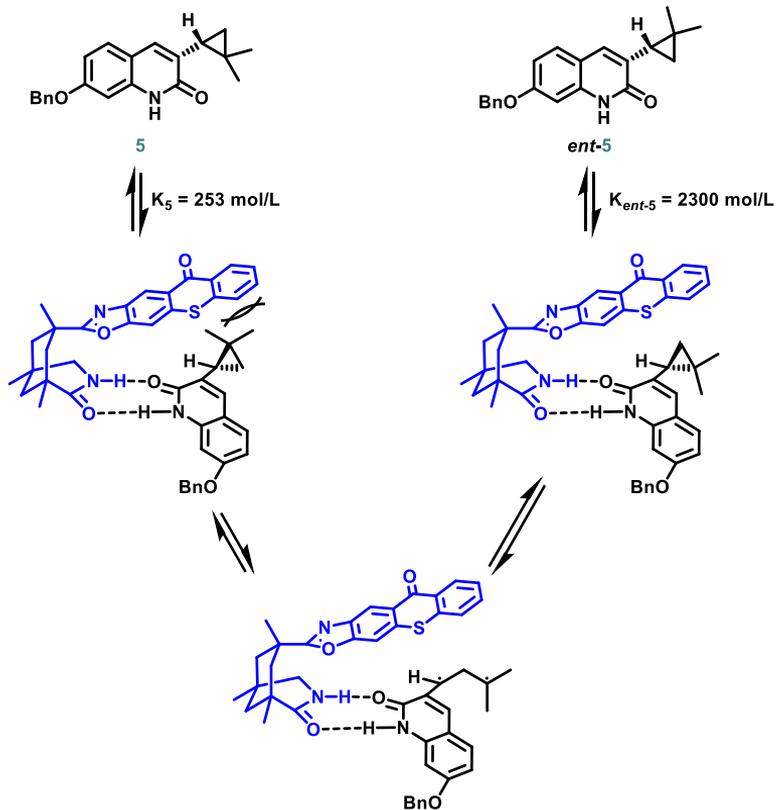


4 under standard condition



rac-5 under standard condition

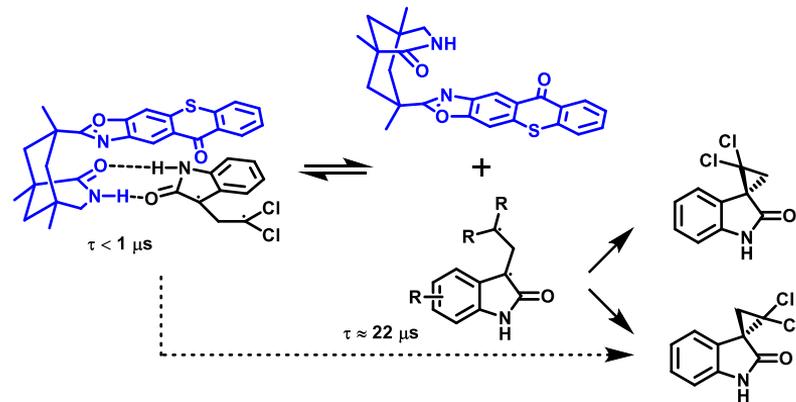
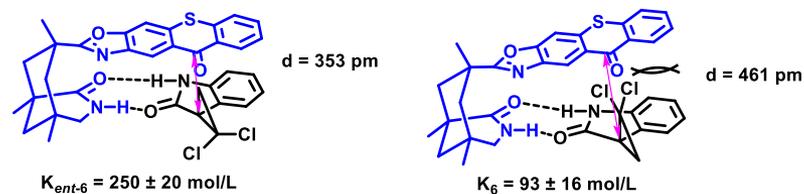
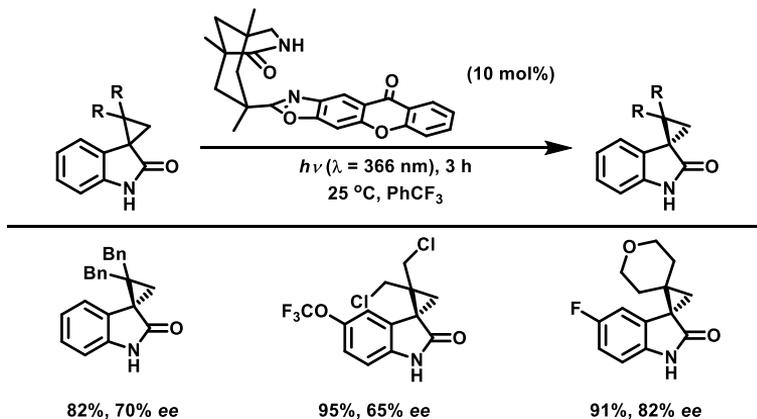
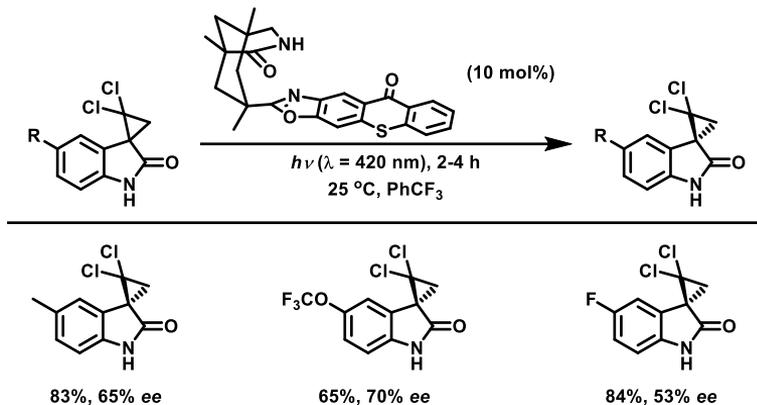
EnT过程去消旋化

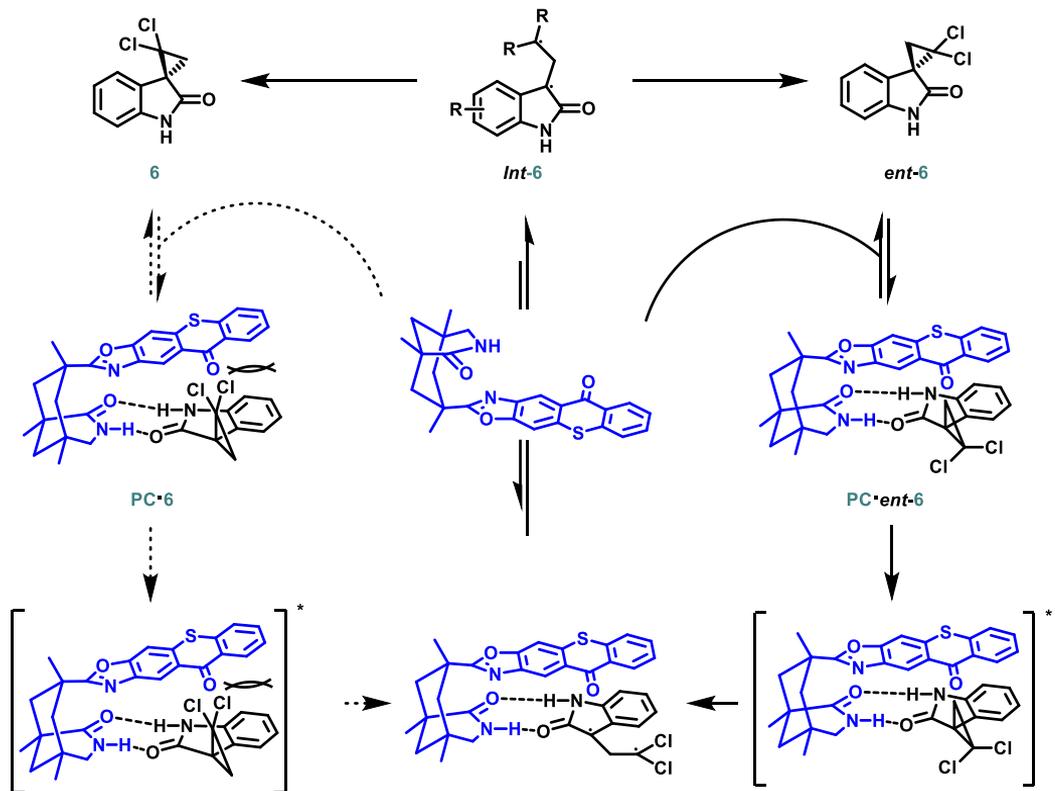


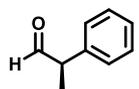
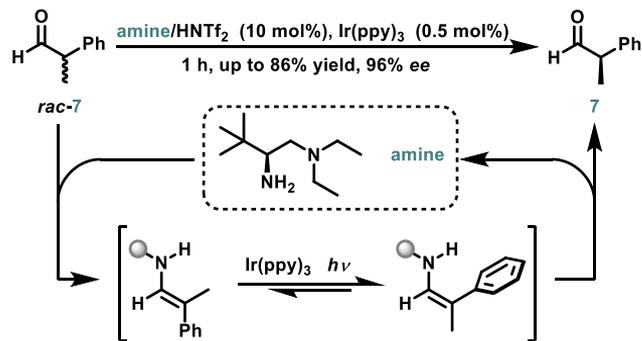
- with thioxanthen-9-one
- with piperylene (c = 15 mM)
- without thioxanthen-9-one
- ▲ with piperylene (c = 30 mM)
- without piperylene

T. Bach *et al.*, *Angew. Chem. Int. Ed.* **2019**, 58, 3538-3541

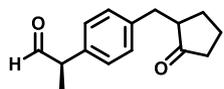
T. Bach *et al.*, *Angew. Chem. Int. Ed.* **2020**, 59, 21640-21647



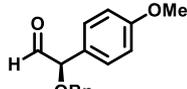




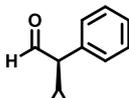
73%, 94% ee



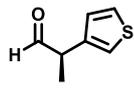
78%, 91% ee



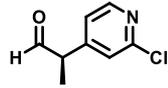
73%, 66% ee



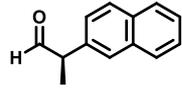
85%, 80% ee



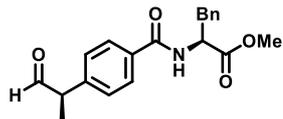
70%, 86% ee



86%, 77% ee



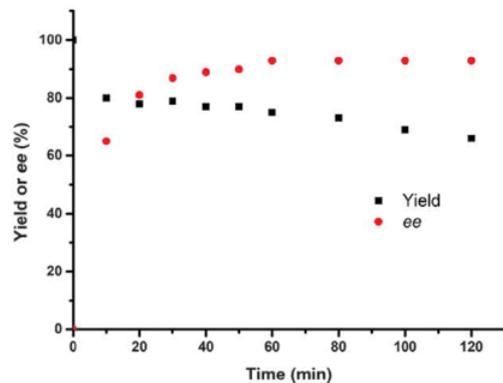
85%, 77% ee



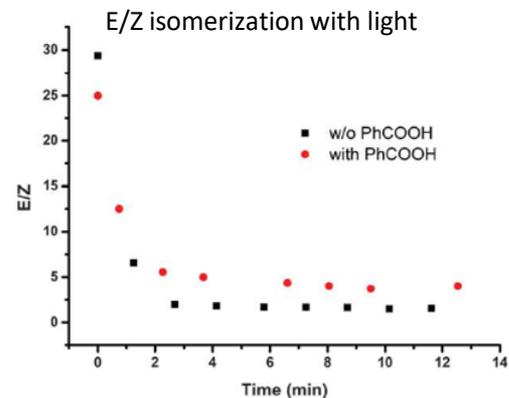
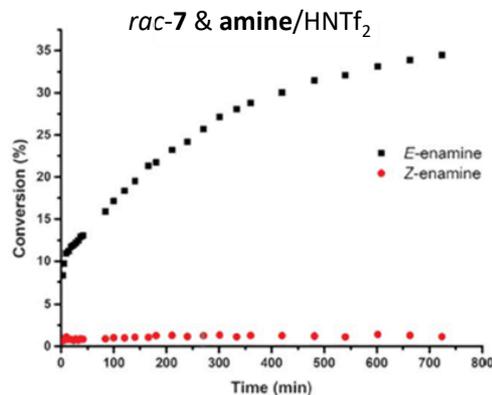
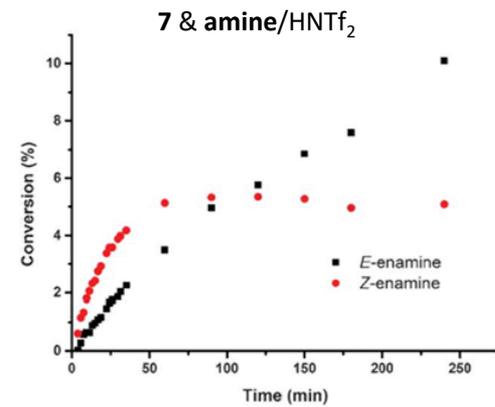
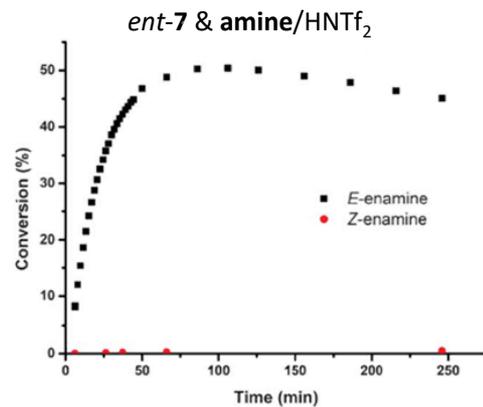
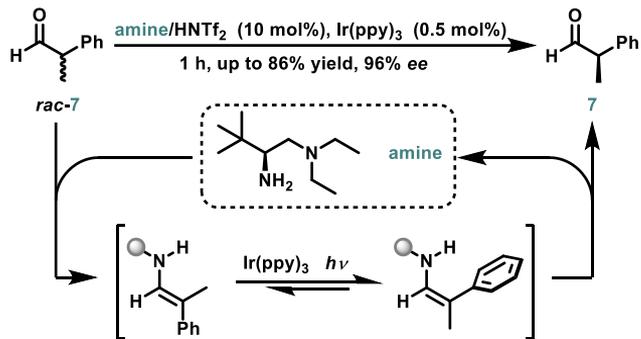
63%, 93/7 dr

Photocatalyst	E _T (kcal/mol)	E _{1/2} ^{PC+/PC*} (V)	ee (%)
Thioxanthone	64.4	+1.18	64
Ir(dFCF ₃ ppy) ₂ dtbbpyPF ₆	61.8	+1.21	73
Ir(ppy)₃	58.1	+0.31	94
Ir(pCF ₃ -ppy) ₃	56.4	+0.59	93
2,4,6-triphenylpyrylium	53.0	+2.02	18
Ru(bpy) ₃ Cl ₂ ·6H ₂ O	46.5	+0.77	39
(<i>E</i>)-enamine	54.2	+0.73	-

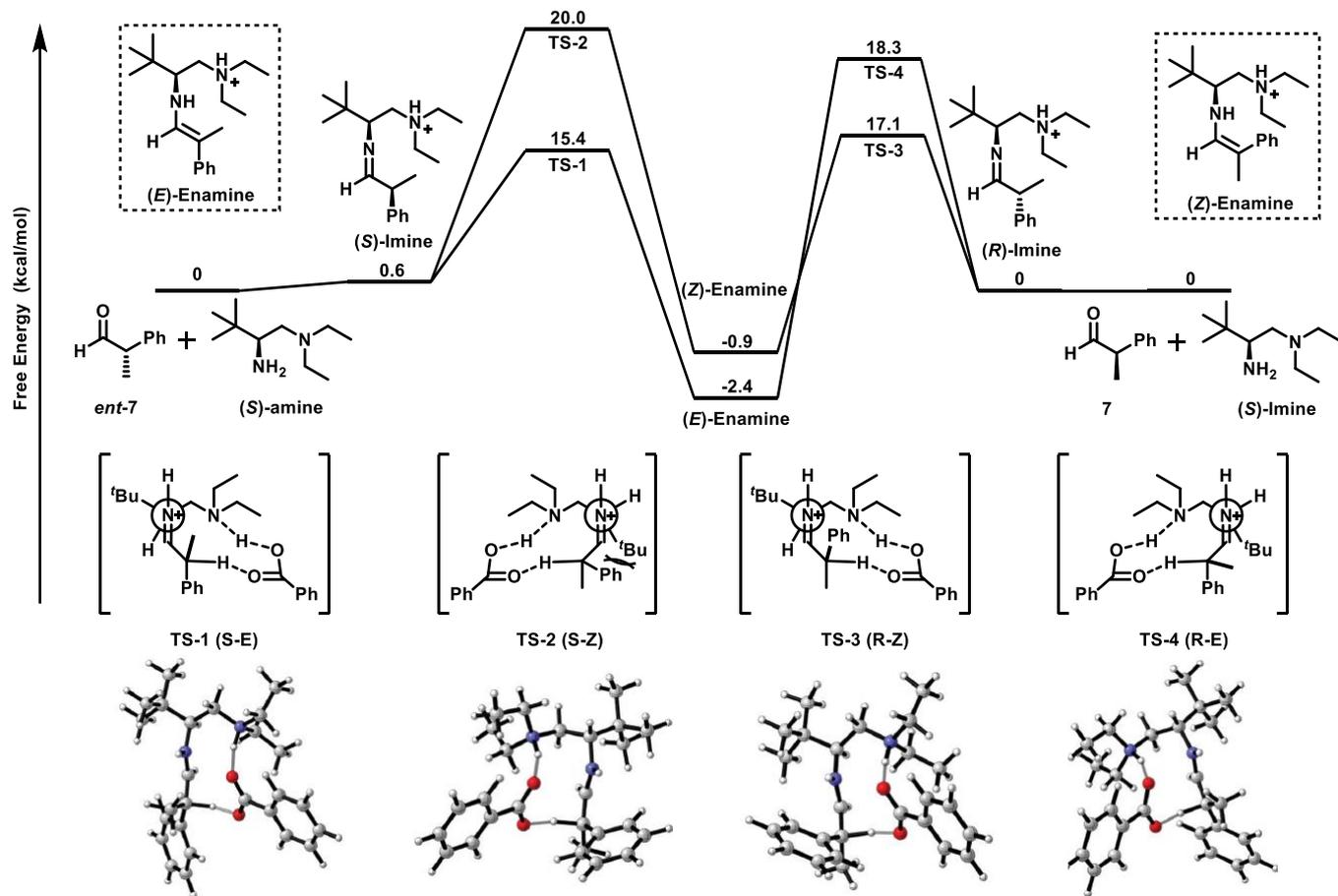
Deracemization curve



EnT过程去消旋化



EnT过程去消旋化

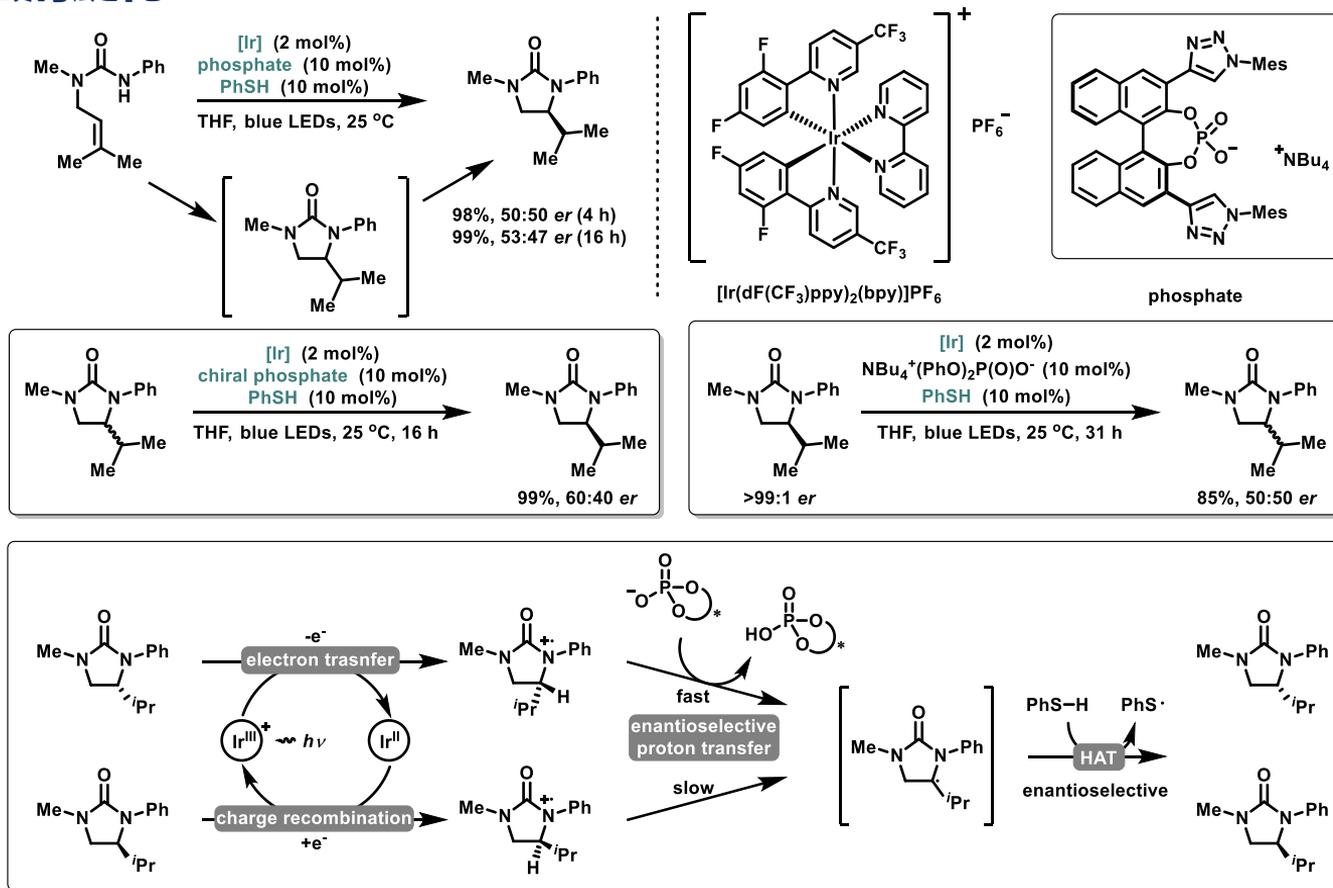


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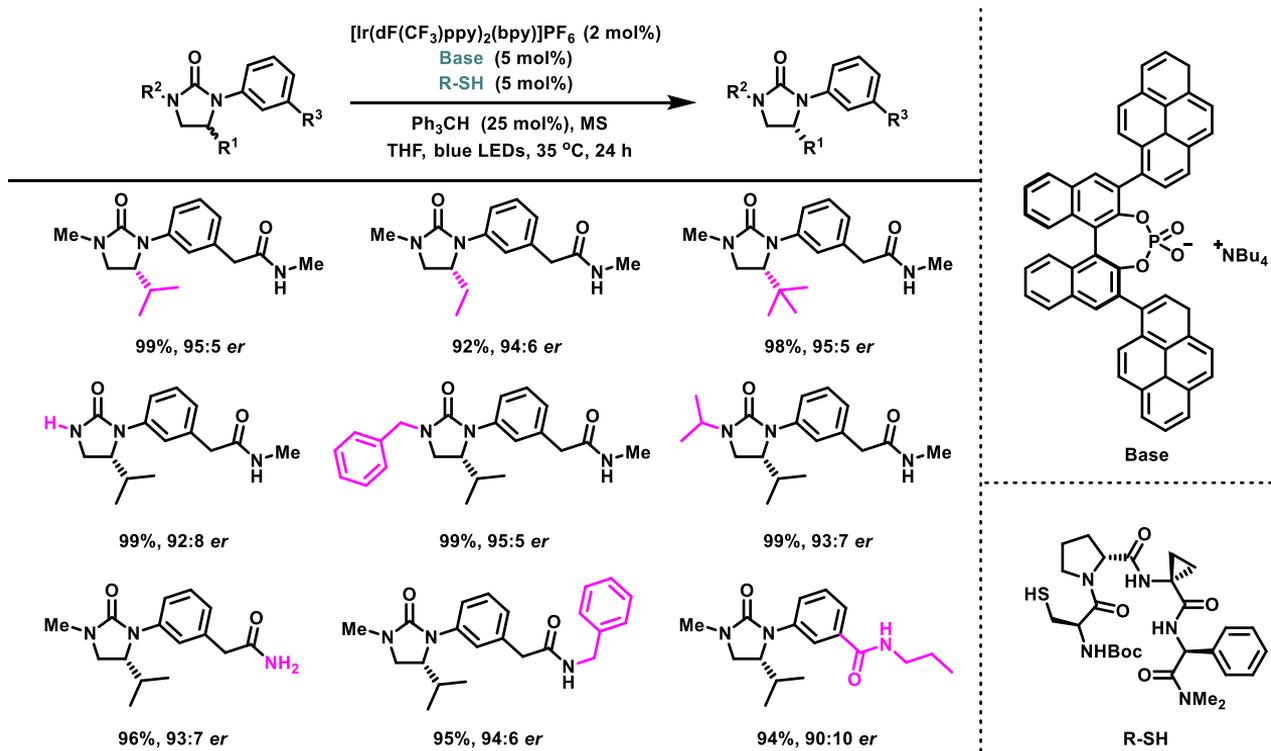
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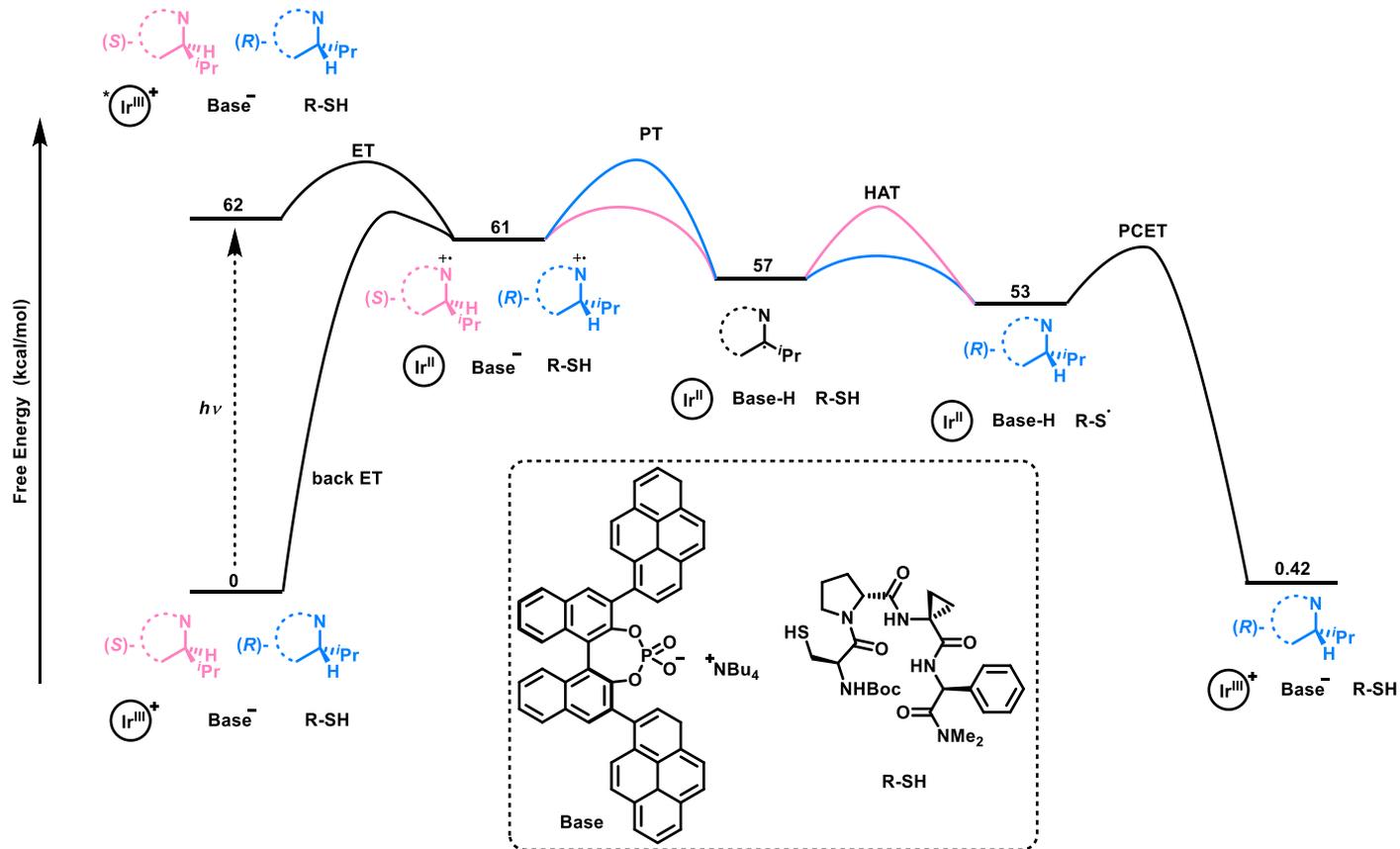
R. R. Knowles *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 13492-13495

S. J. Miller & R. R. Knowles *et al.*, *Science* **2019**, *366*, 364-369

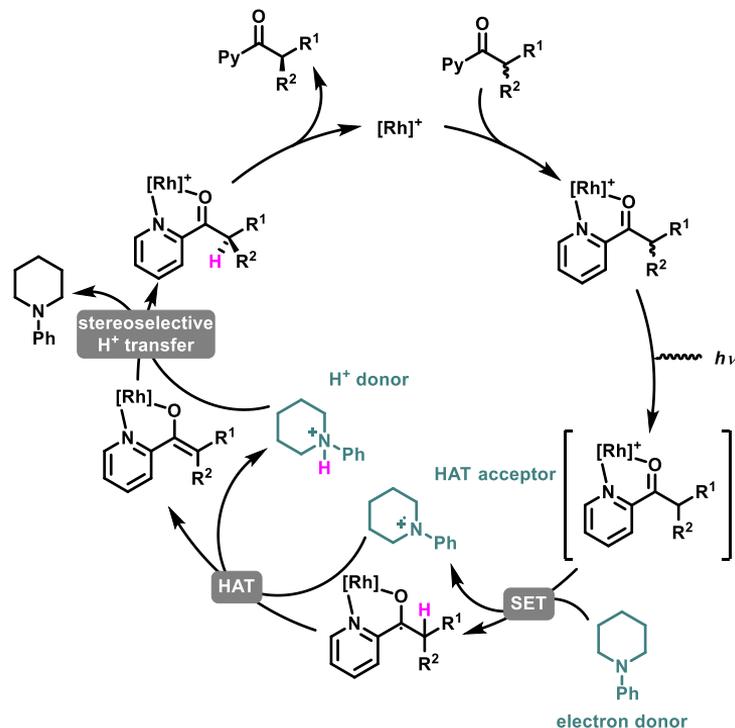
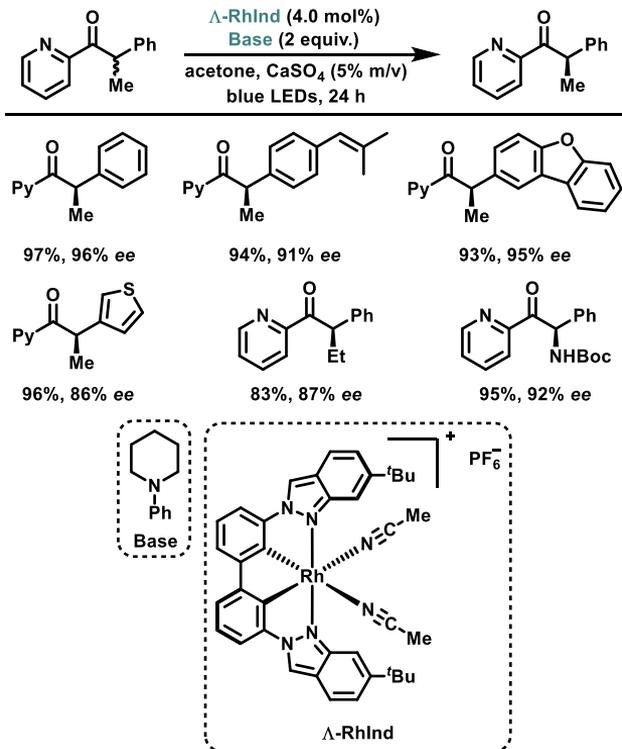
SET过程去消旋化

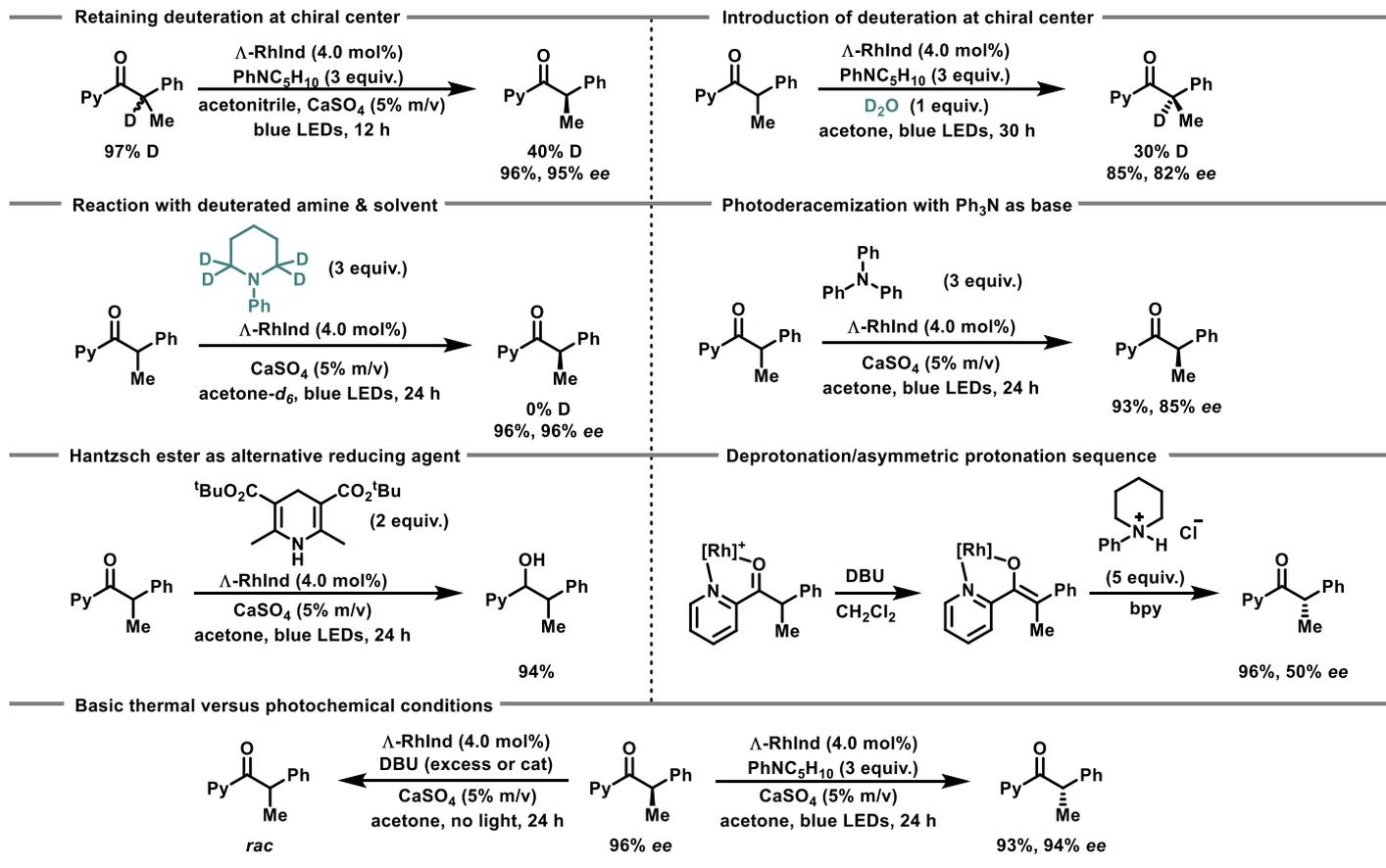


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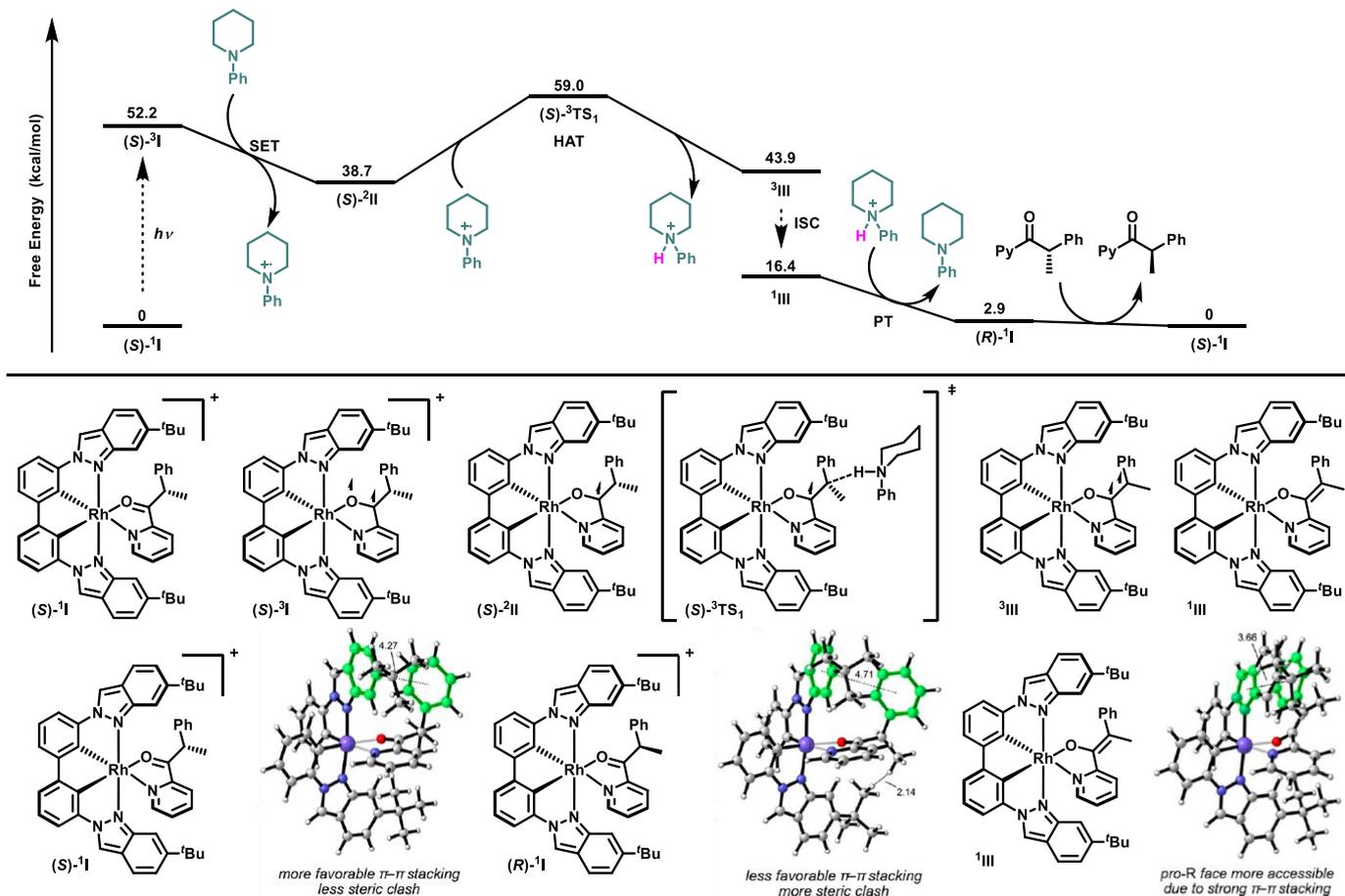


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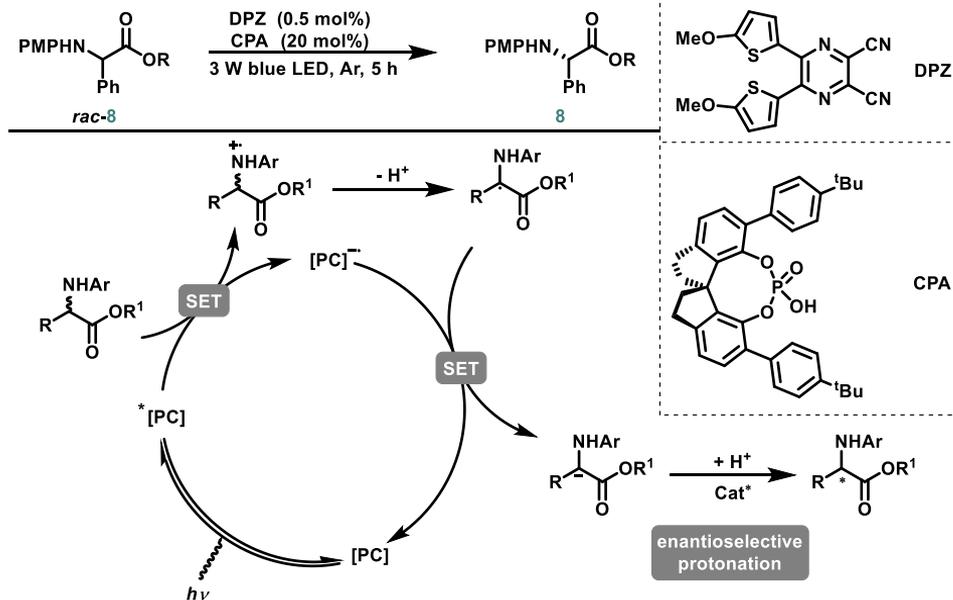




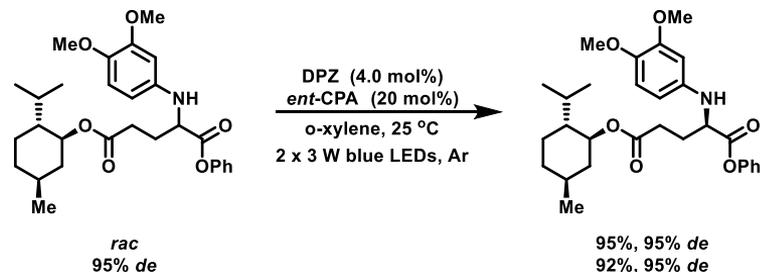
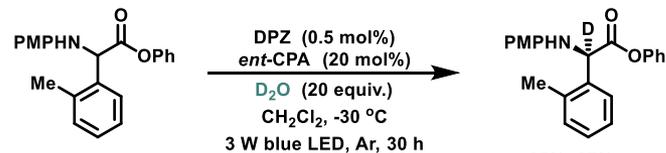
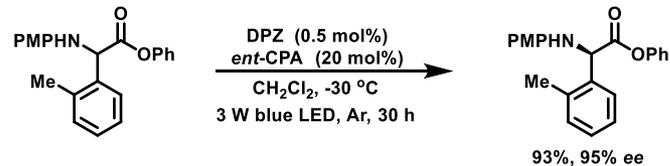
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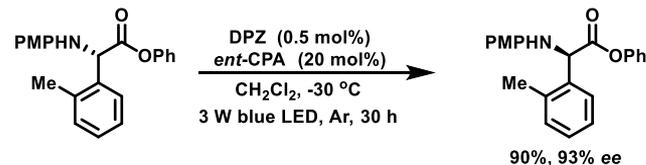
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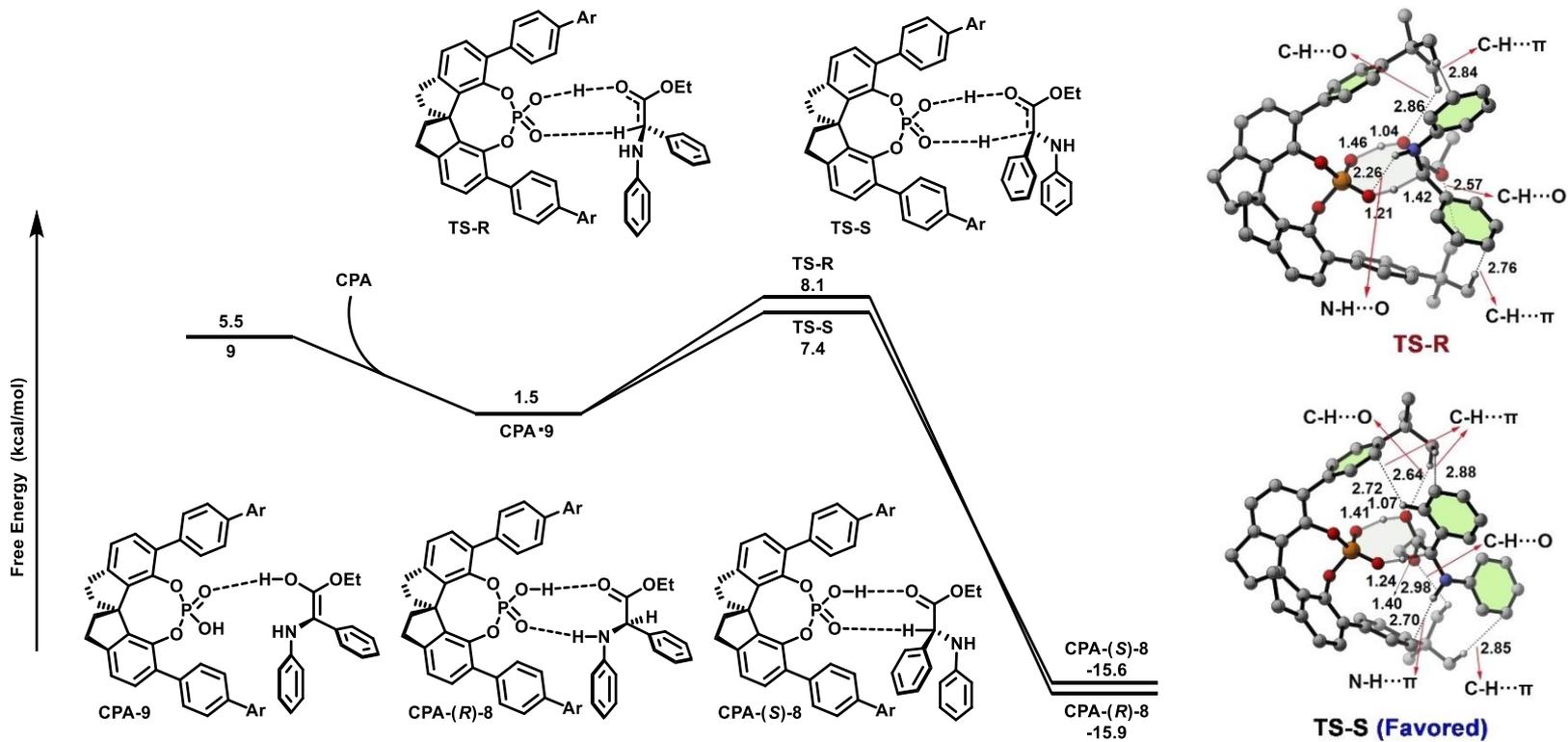
reaction with racemic substrate



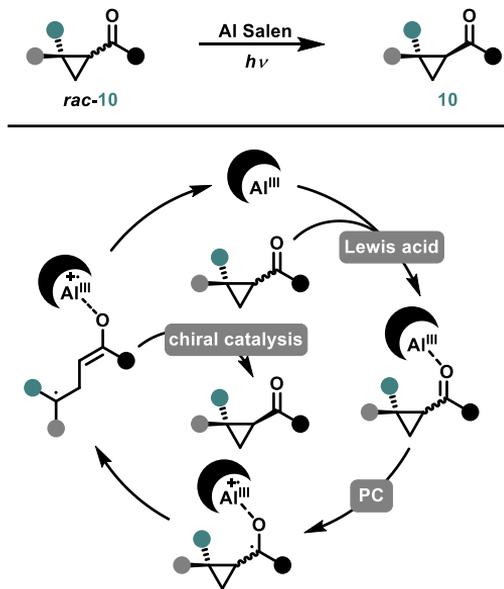
reaction with chiral substrate



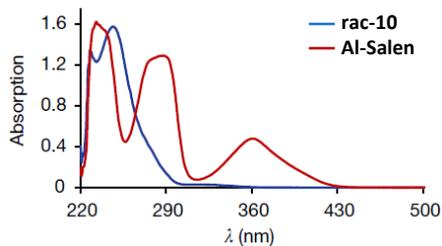
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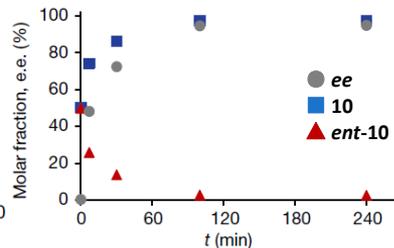
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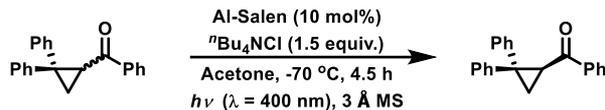
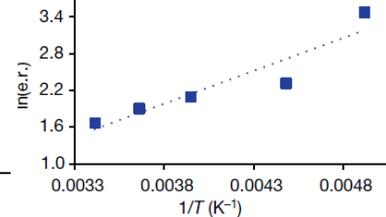
Ultraviolet-visible spectroscopy



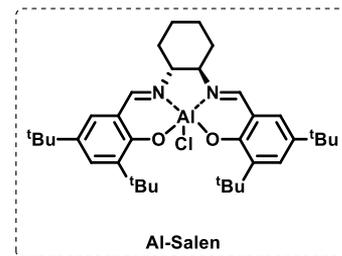
Reaction monitoring



Temperature effects



Entry	light	cat	MS	yield (%)	er
1	×	√	√	quant.	50:50
2	√	×	√	quant.	50:50
3	√	√	×	96	72:28

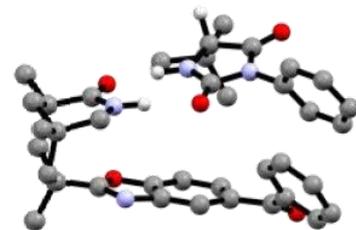
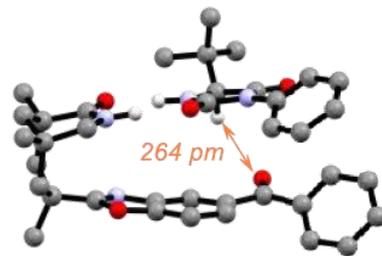
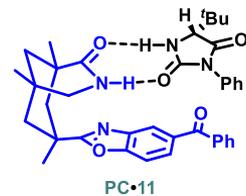
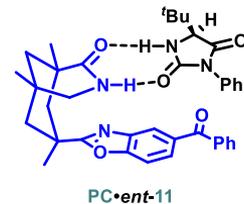
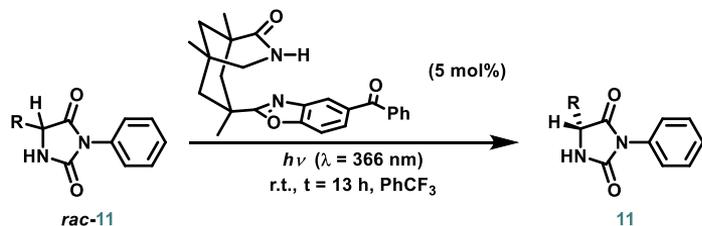
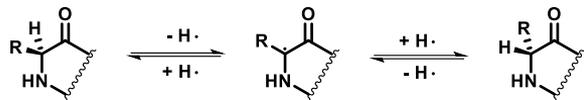


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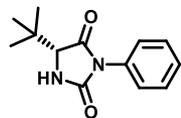
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- 1/ 研究背景
- 2/ EnT过程去消旋化
- 3/ SET过程去消旋化
- 4/ HAT过程去消旋化
- 5/ 总结与展望

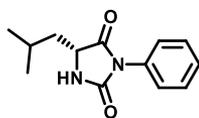
HAT过程去消旋化



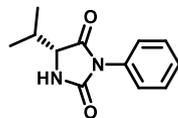
$c = 10$ mM



quant., 95% ee

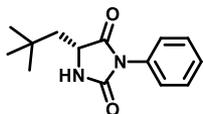


86%, 93% ee

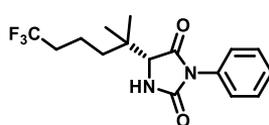


87%, 83% ee

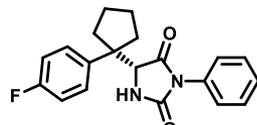
$c = 2.5$ mM



97%, 96% ee



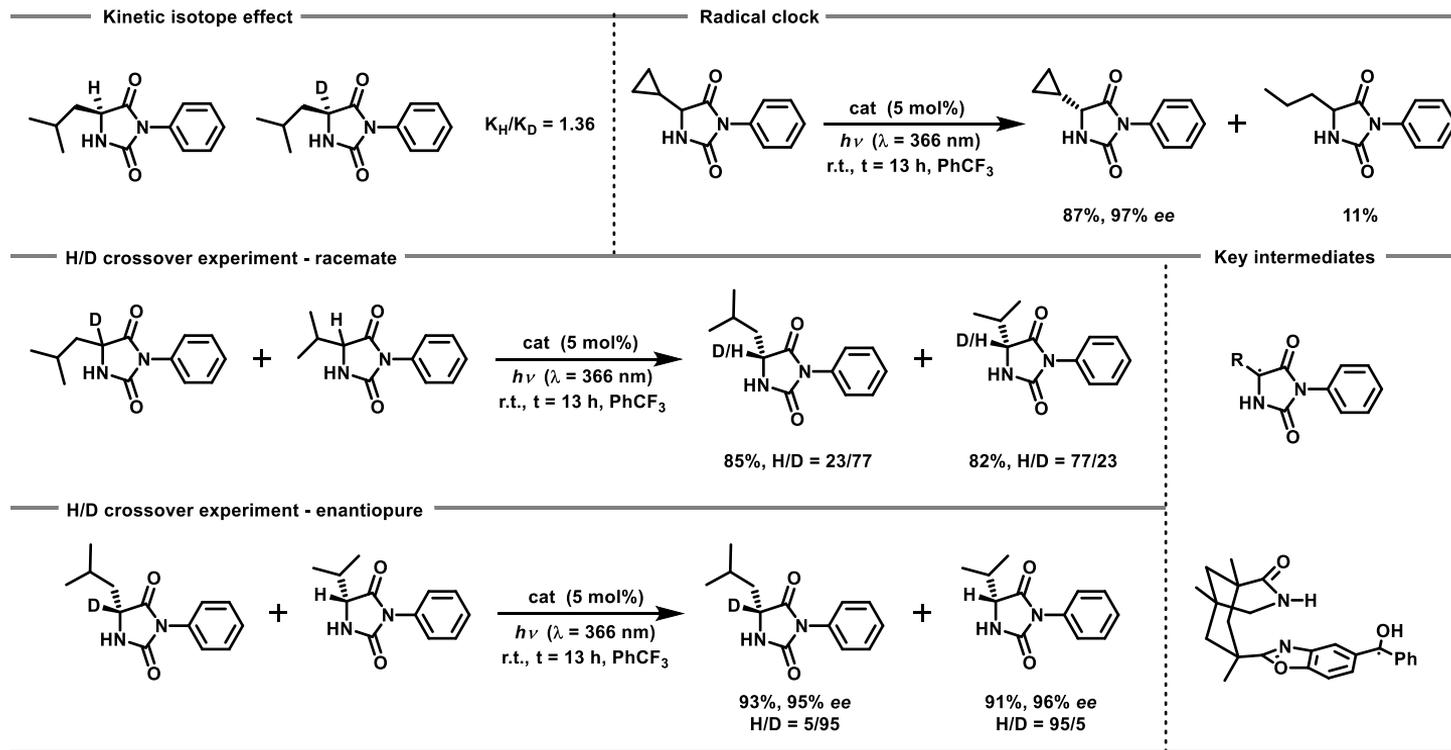
88%, 92% ee



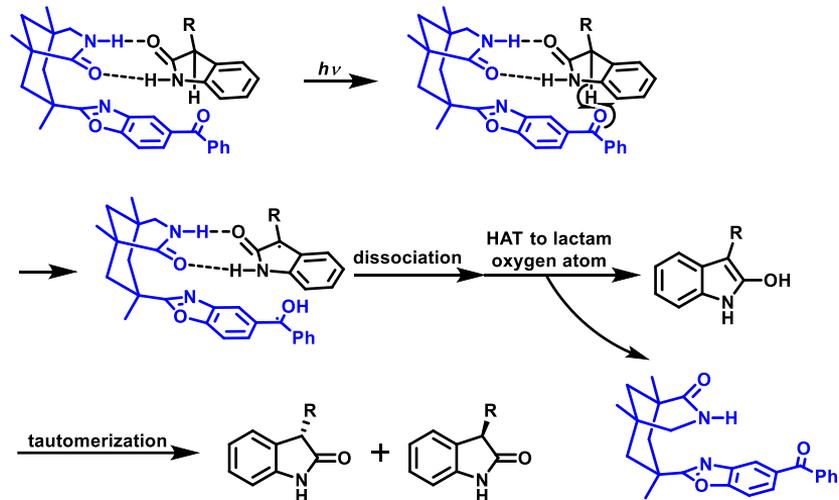
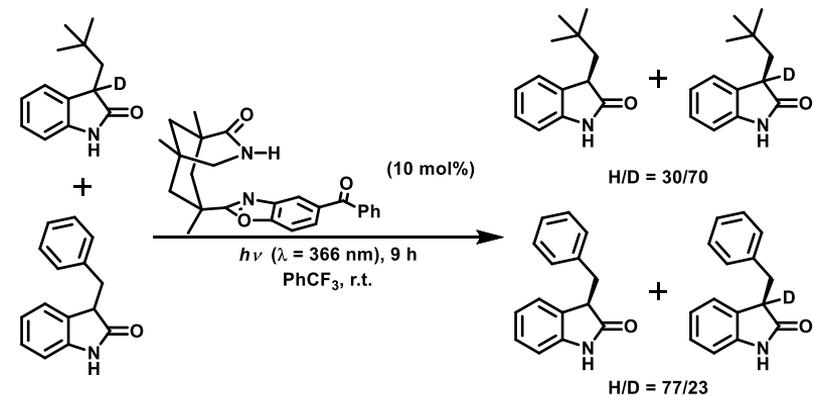
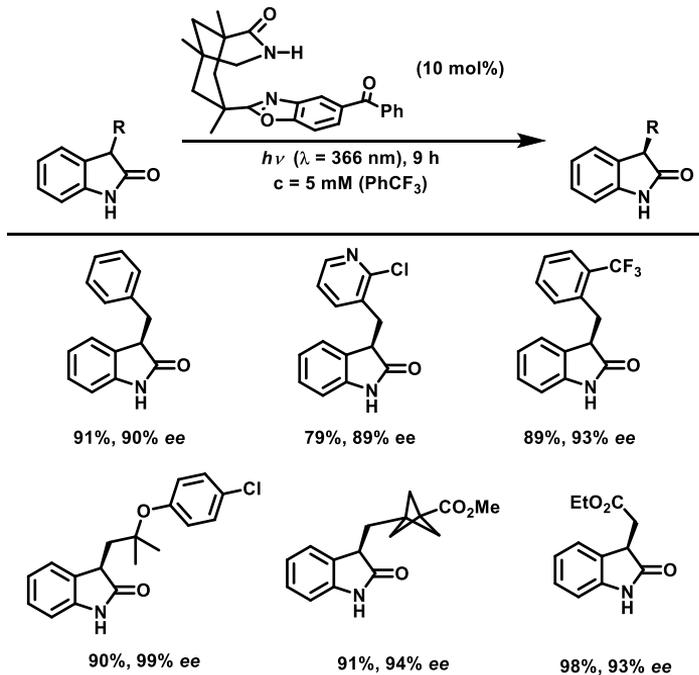
76%, 91% ee

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C. Bannwarth, P. Nuernberger & T. Bach *et al.*, *J. Am. Chem. Soc.* **2023**, *145*, 2354-2363



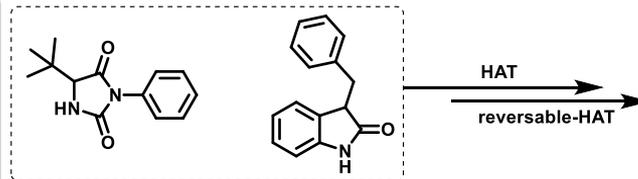
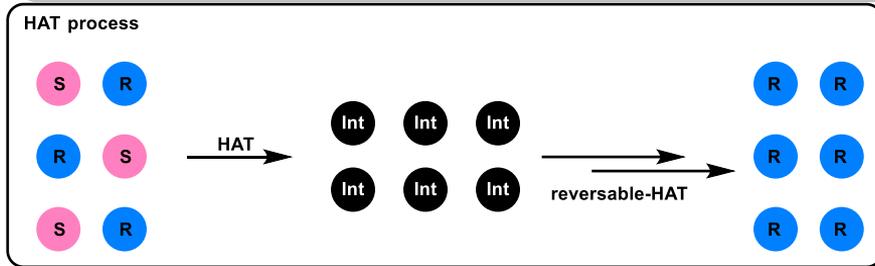
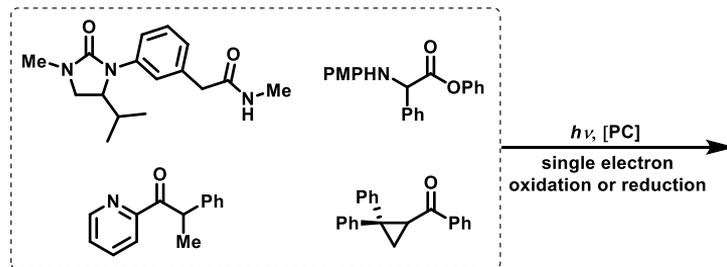
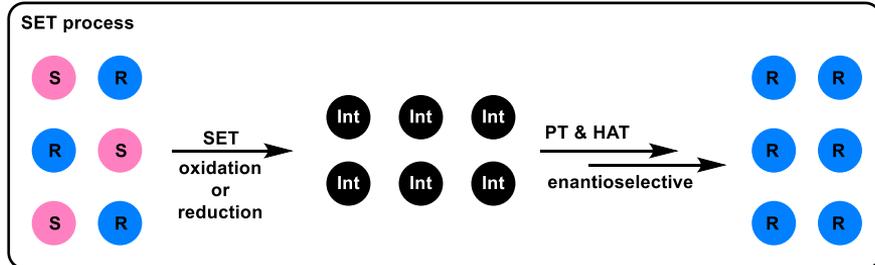
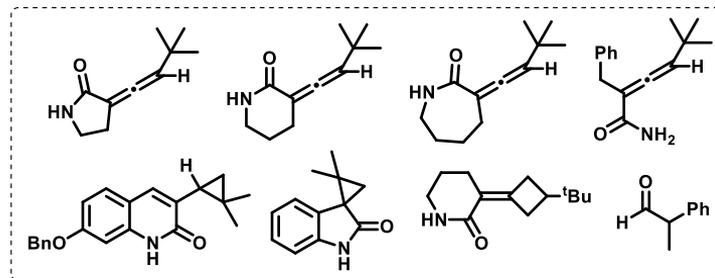
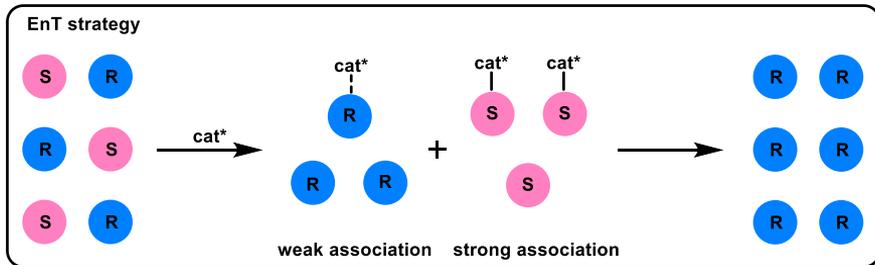
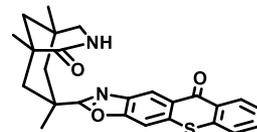
HAT过程去消旋化



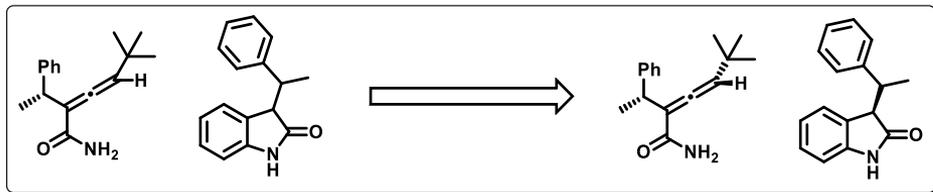
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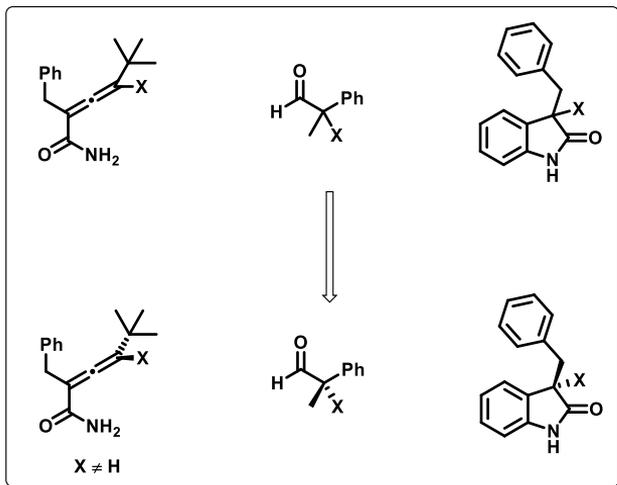
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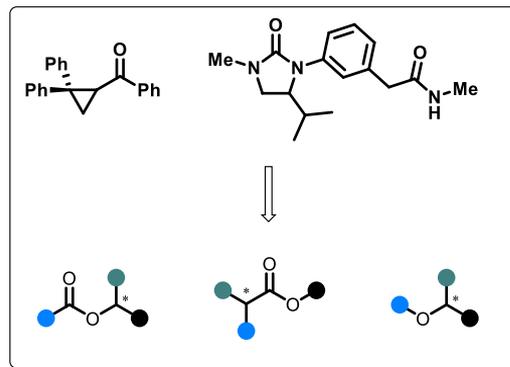
1. 多个手性元素化合物的去消旋化



2. 对于无C-H键的中心手性及轴手性化合物的去消旋化



3. 扩展底物类型





**请各位老师同学批评指正！
谢谢！**

汇报人：黄言恺

指导老师：麻生明 教授

汇报日期：2023.9.22