

Literature Report VIII

Design of Stable Chiral Aminosulfonium Ylides and Their Catalytic Asymmetric Synthesis

Reporter: Qing-Xian Xie

Checker: Gao-Wei Wang

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Bao, W.; Wang, X.-J.; Wang, S.-H.; Chen, S.-W.; Liu, H.-H.; Xiang, S.-H; [Tan, B.](#)

Angew. Chem. Int. Ed. **2024**, e202412508

CV of Prof. Bing Tan

Background:



- ❑ **1997-2001** B. S., Hunan University of Science and Technology
- ❑ **2001-2005** M. S., Xiamen University
- ❑ **2005-2010** Ph. D., Nanyang Technological University
- ❑ **2010-2012** Postdoc., The Scripps Research Institute
- ❑ **2012-2018** Tenure-Track Associate Professor, SUSTC
- ❑ **2018-Now** Professor, SUSTC

Research:

- ❑ Asymmetric axis chiral chemistry
- ❑ Organocatalytic multicomponent reactions
- ❑ Discovery and synthesis of chiral drug molecules

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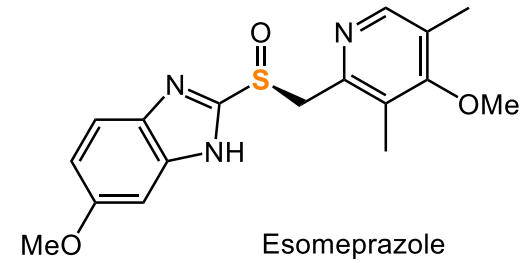
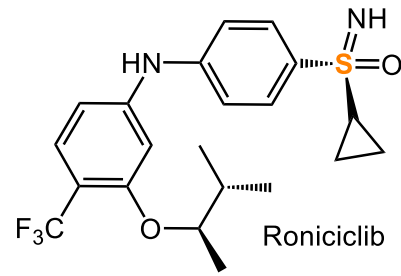
2 Enantioselective Synthesis of *S*-Stereogenic Compounds

3 Catalytic Asymmetric Synthesis of Sulfonium Ylides

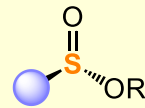
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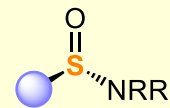
Selected Structures with a Chirality at S-Center



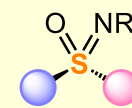
Sulfoxides
亚砷



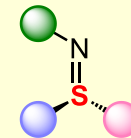
Sulfinate Esters
亚磺酸酯



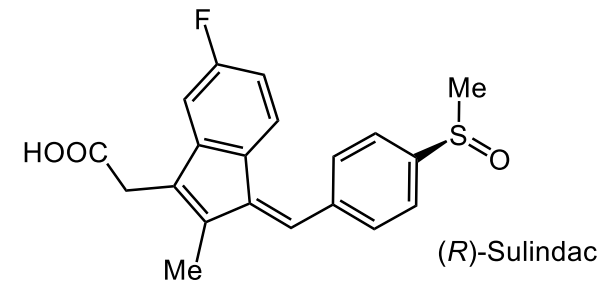
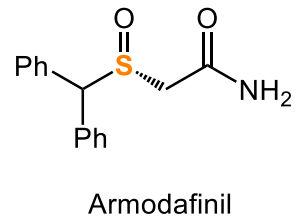
Sulfinamide
亚磺酰胺



Sulfoximines
亚砷亚胺

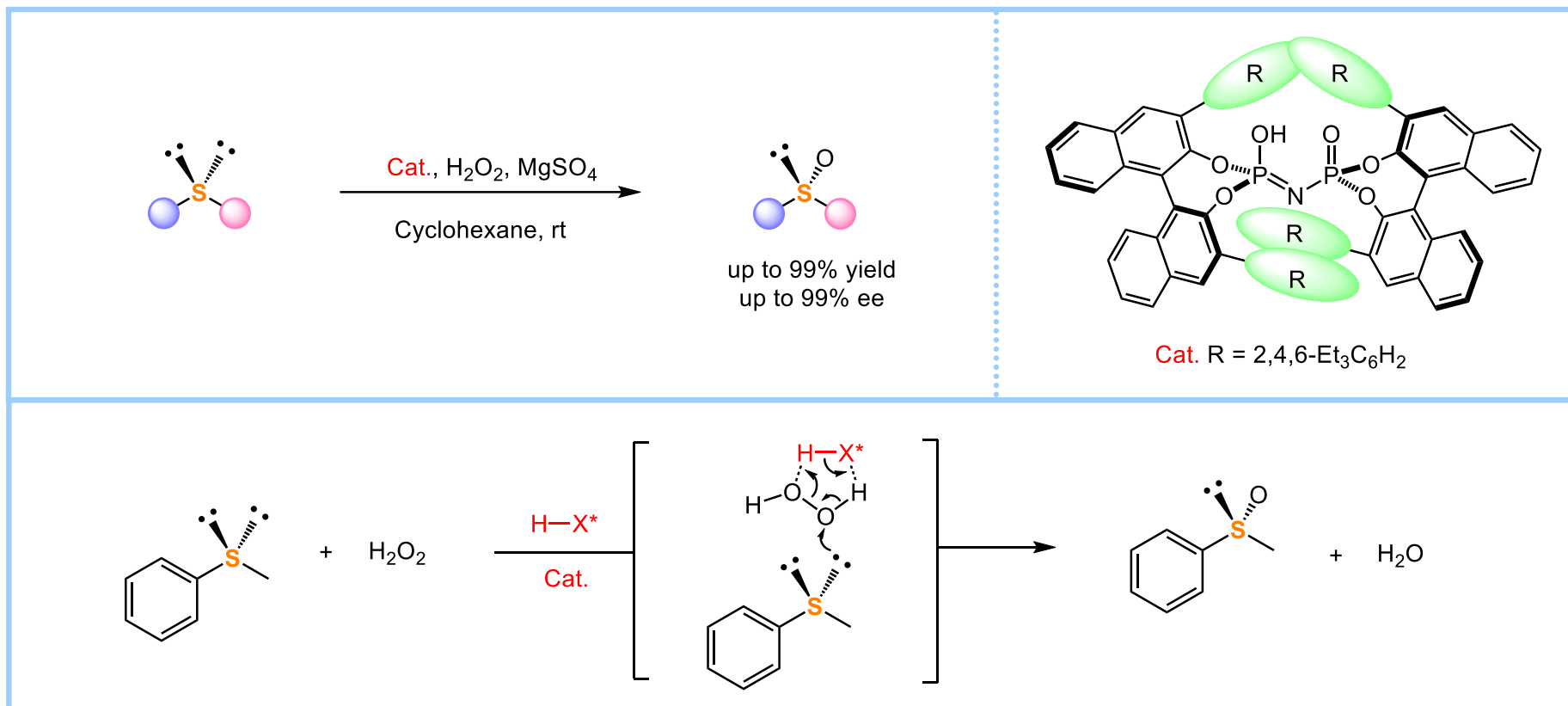


Sulfenamides
硫亚胺



Catalytic Asymmetric Synthesis of Sulfoxides

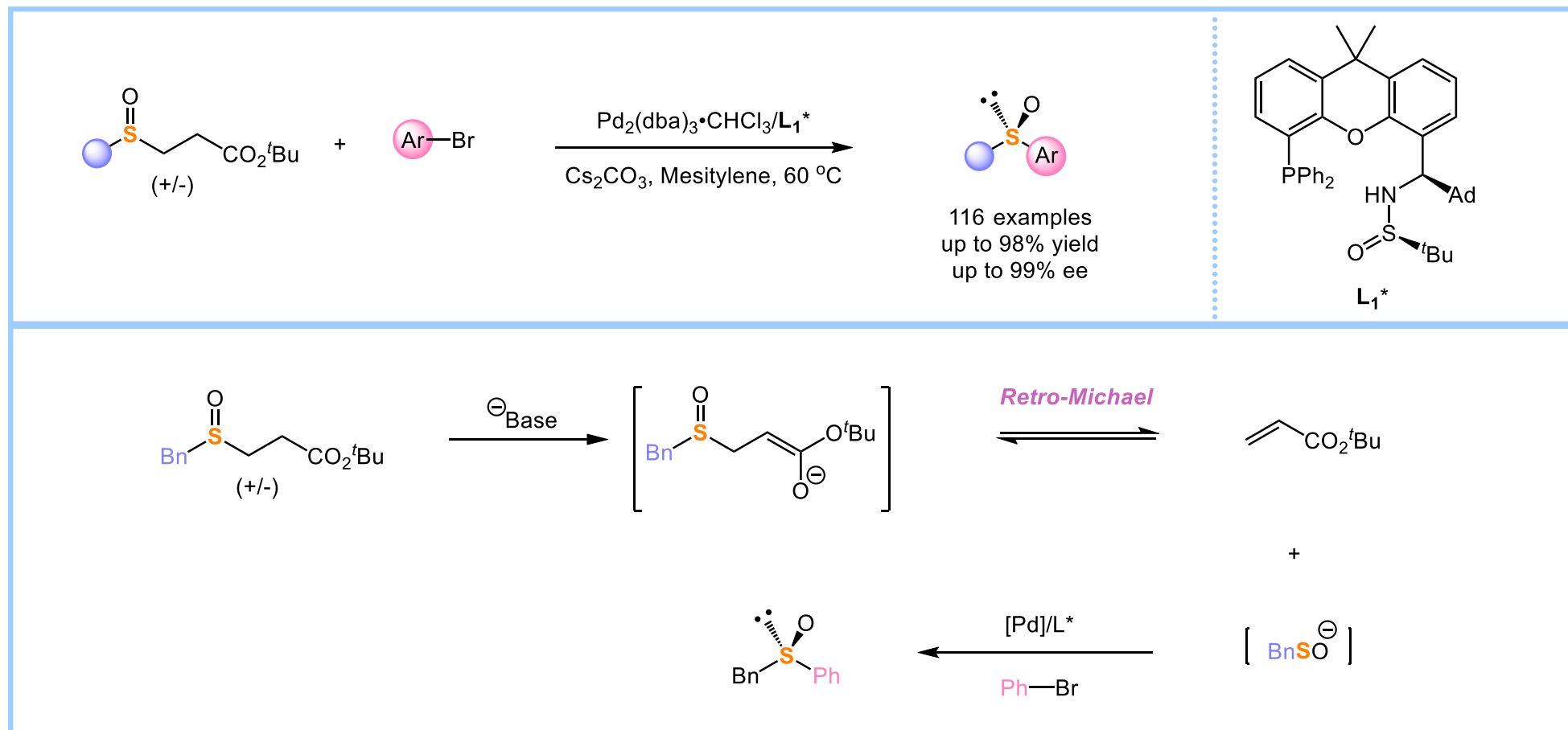
Organocatalytic Asymmetric Oxidation



Liao, S.; Coeic, I.; Wang, Q.; List, B.* *J. Am. Chem. Soc.* **2012**, *134*, 10765-10768

Catalytic Asymmetric Synthesis of Sulfoxides

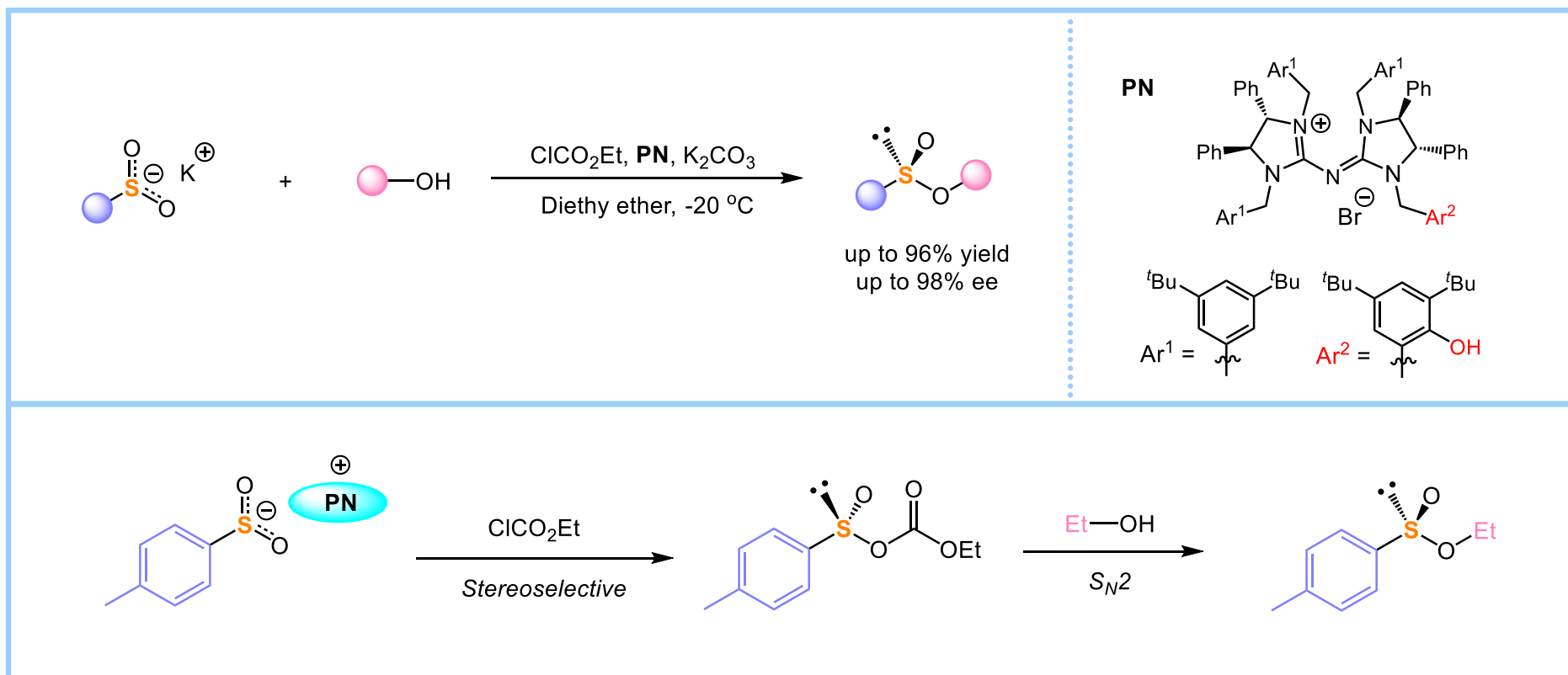
Transition-metal-catalyzed Arylations via Sulfenate Anions



Wang, L.; Chen, M.; Zhao, P.; Li, W.; Zhang, J.* *J. Am. Chem. Soc.* **2018**, *140*, 3467-3473

Catalytic Asymmetric Synthesis of Sulfinic Esters

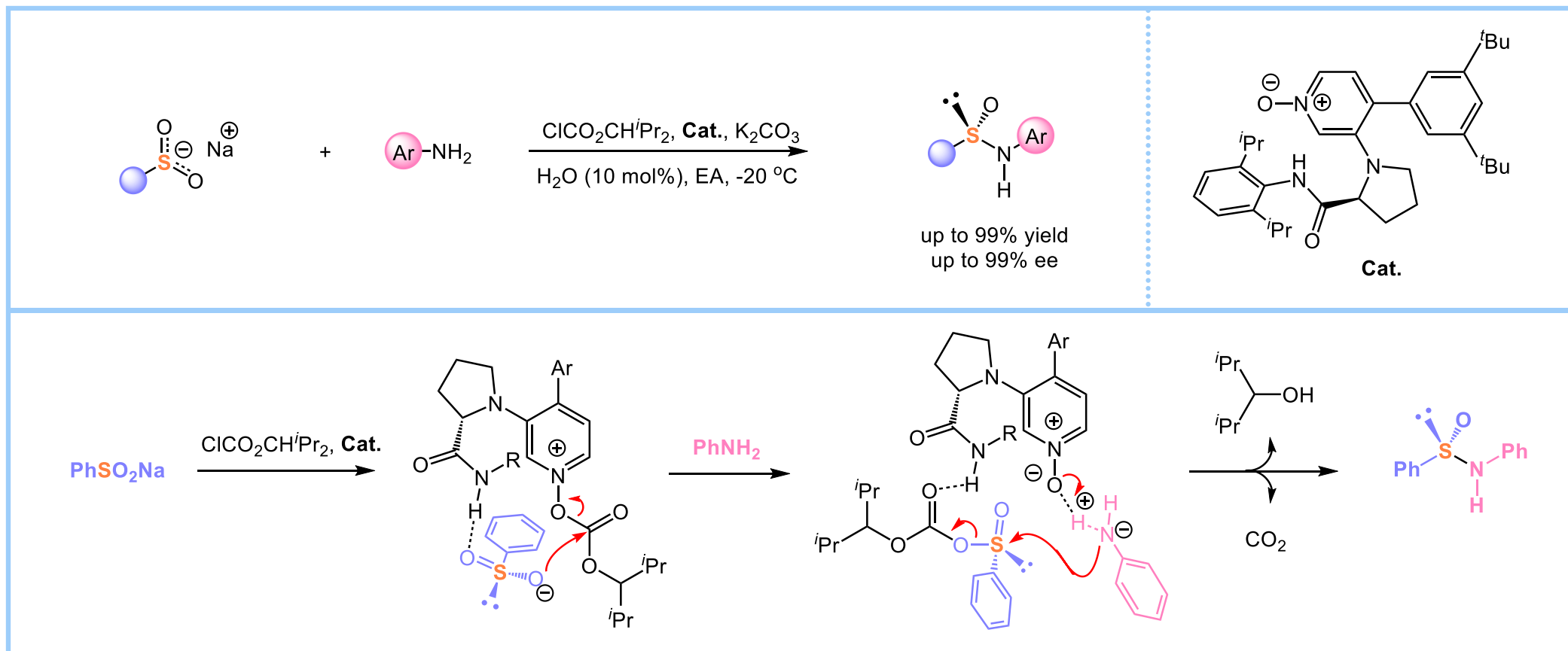
Synthesis of Chiral Sulfinic Esters by Asymmetric Condensation



Zhang, X.; Ang, E. C. X.; Yang, Z.; Kee, C. W.; Tan, C.-H.* *Nature* **2022**, 604, 298-303

Catalytic Asymmetric Synthesis of Sulfinamides

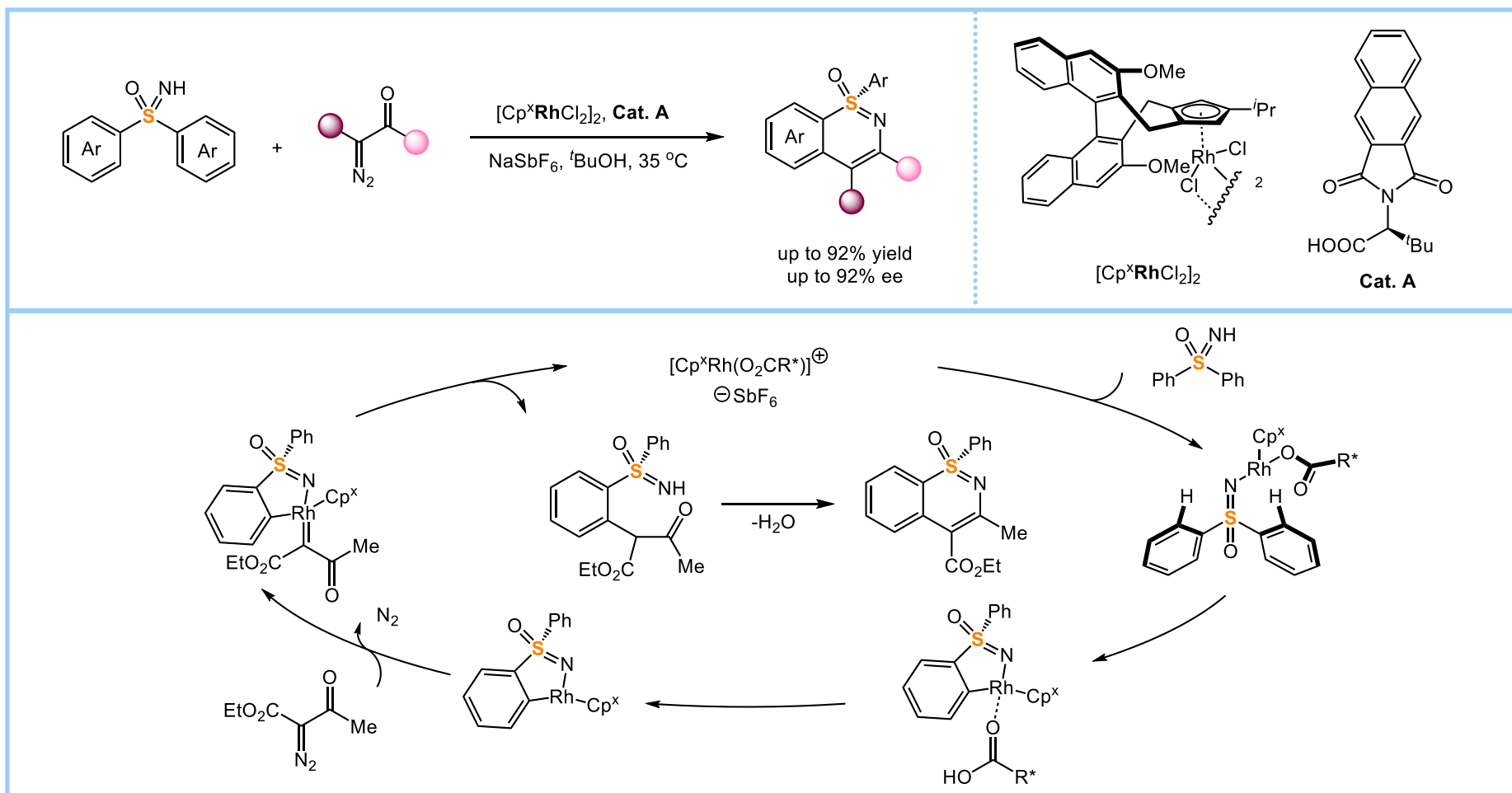
Synthesis of Chiral Sulfinamides by Asymmetric Condensation



Wei, T.; Wang, H.-L.; Tan, Y.;* Xie, M.-S.;* Guo, H.-M.* *Nat. Chem.* **2024**, *16*, 1301-1311

Catalytic Asymmetric Synthesis of Sulfoximines

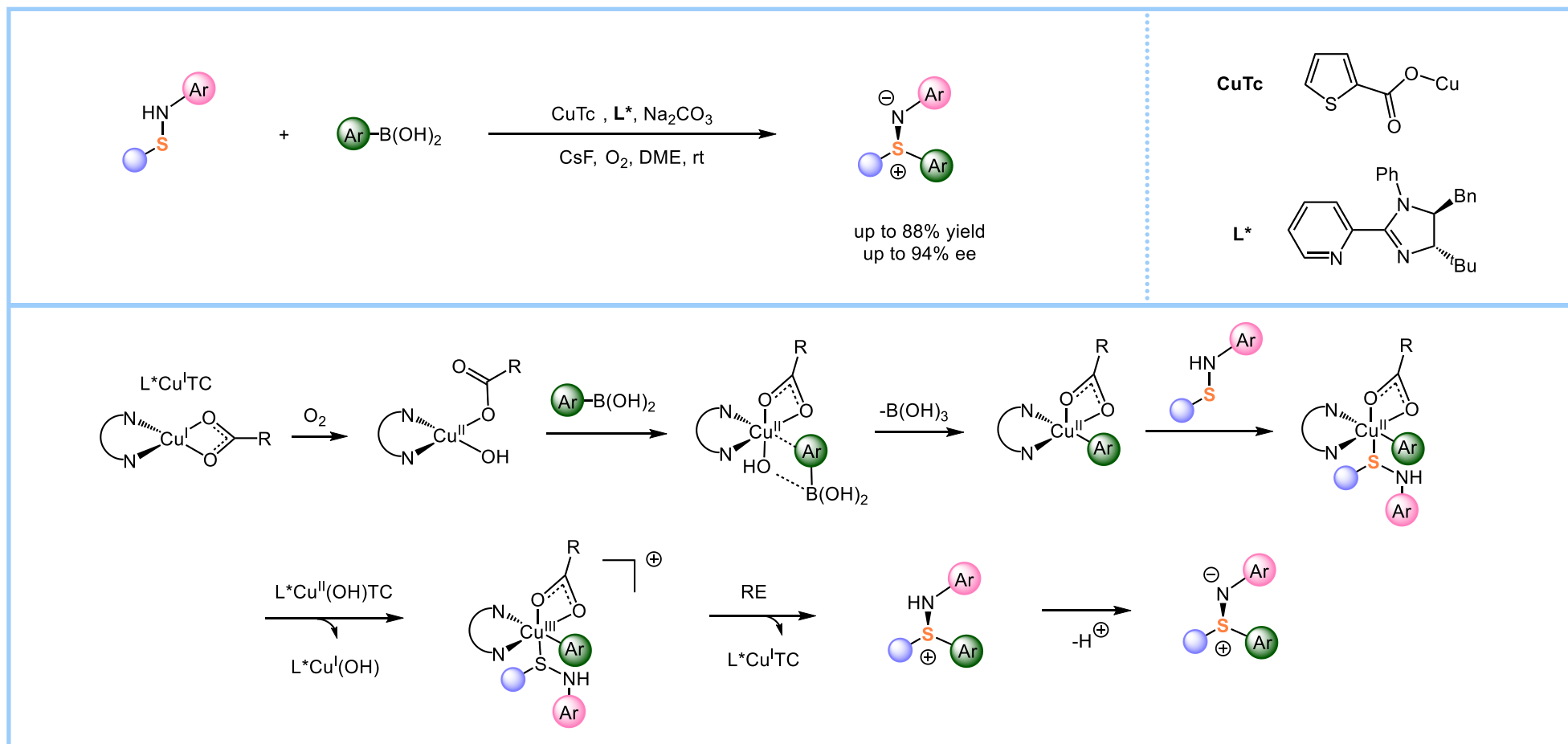
Synthesis of Chiral Sulfoximines by Rh-catalyzed C-H Functionalization



Sun, Y.; Cramer, N.* *Angew. Chem. Int. Ed.* **2018**, *57*, 15539-15543

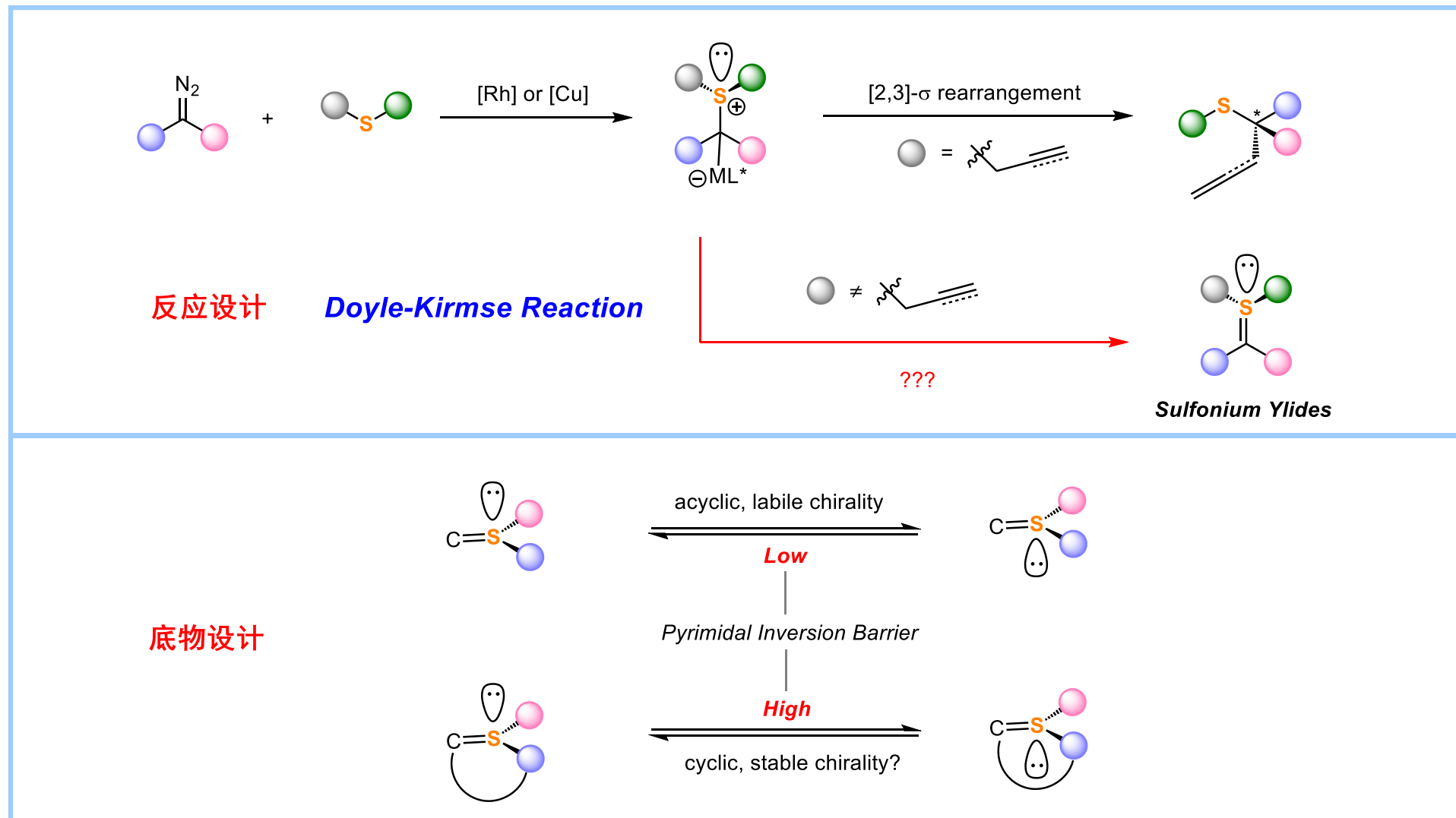
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Enantioselective Chan-Lam S-arylation of Sulfenamides



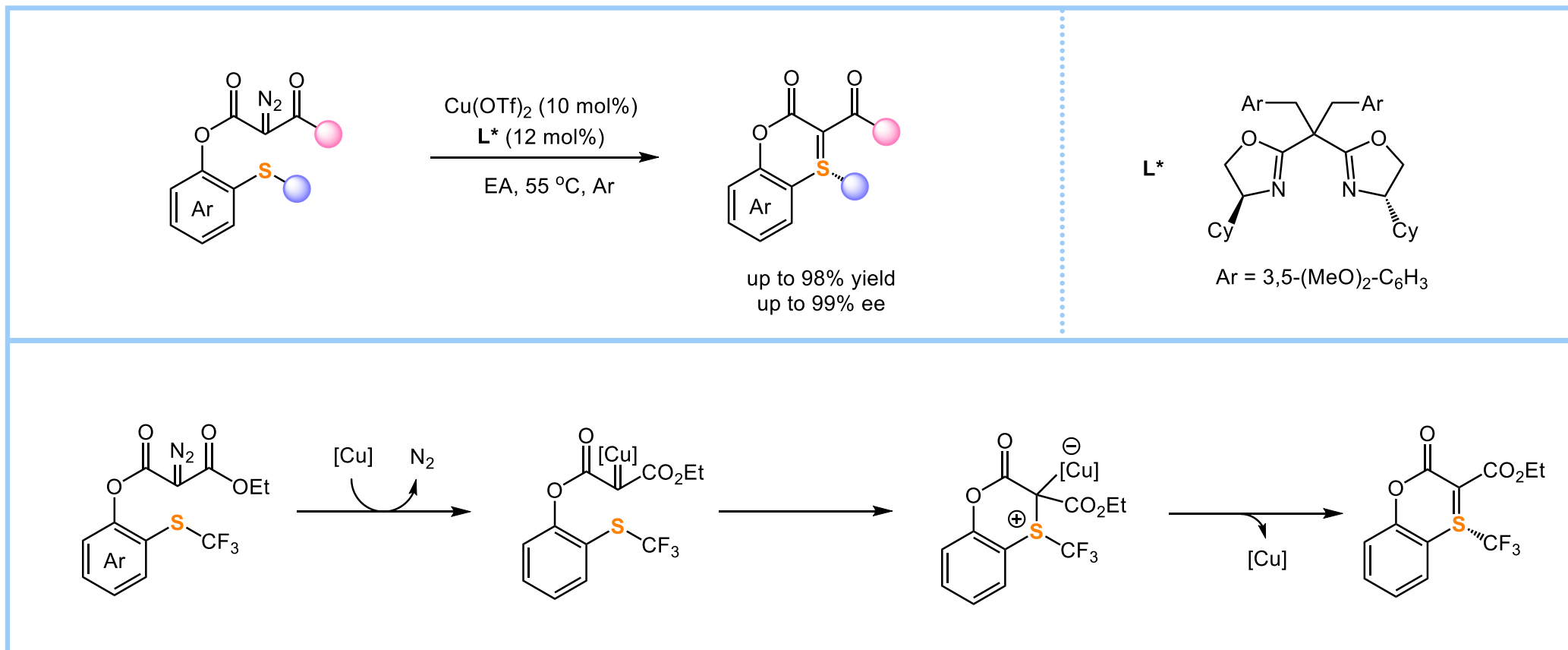
Liang, Q.; Zhang, X.; Xu, Z.; Kozlowski, M. C.*; Jia, T.* *Nat. Catal.* **2024**, *10*, doi.org/10.1038/s41929-024-01213-5

Introduction



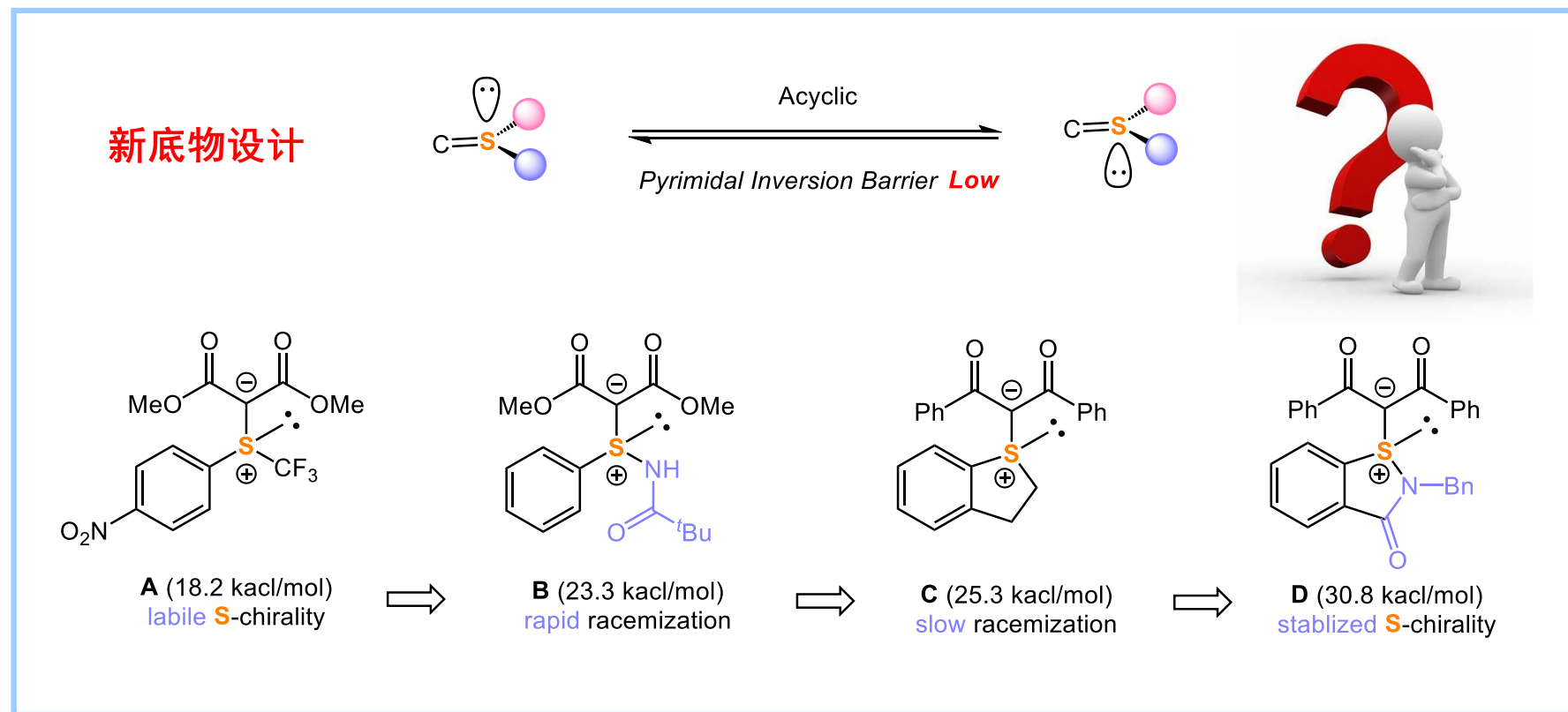
Catalytic Asymmetric Synthesis of Sulfonium Ylides

Enantioselective Synthesis of **Cyclic** Sulfonium Ylides

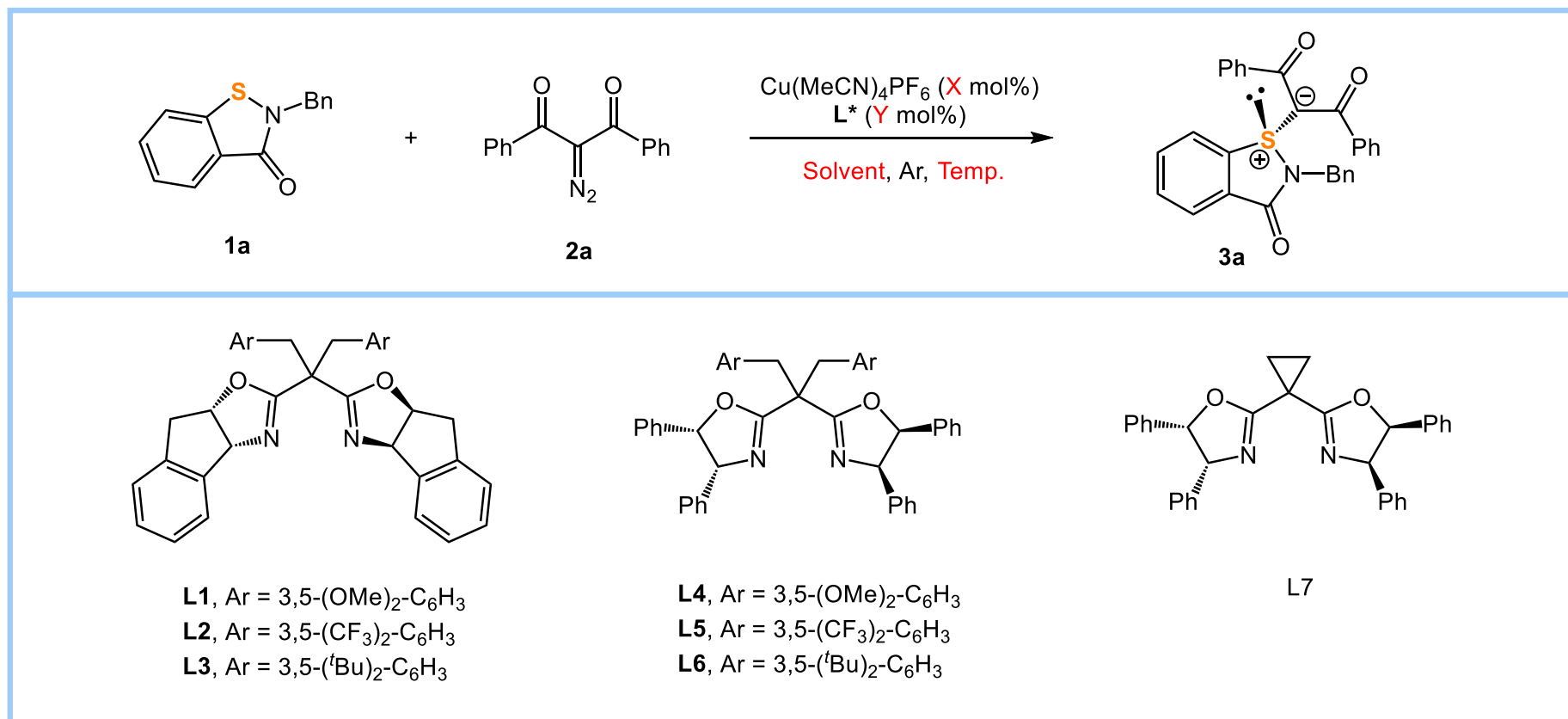


Wang, X.-J.; Liu, H.-H.; Cheng, J. K.; Xiang, S.-H.*; Tan, B.* *Chem* **2023**, 9, 1495-1504

Project Synopsis



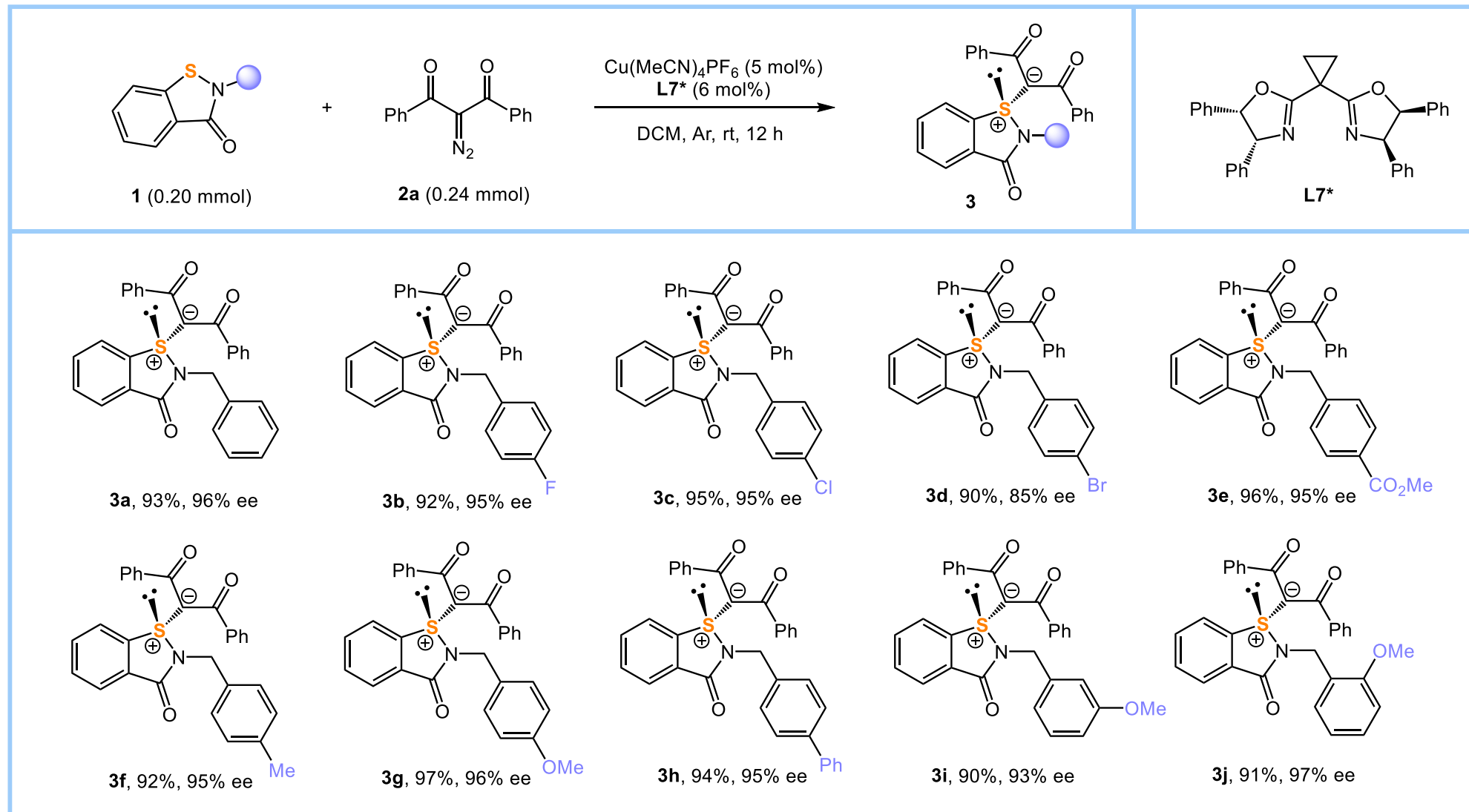
Optimization of Reaction Conditions



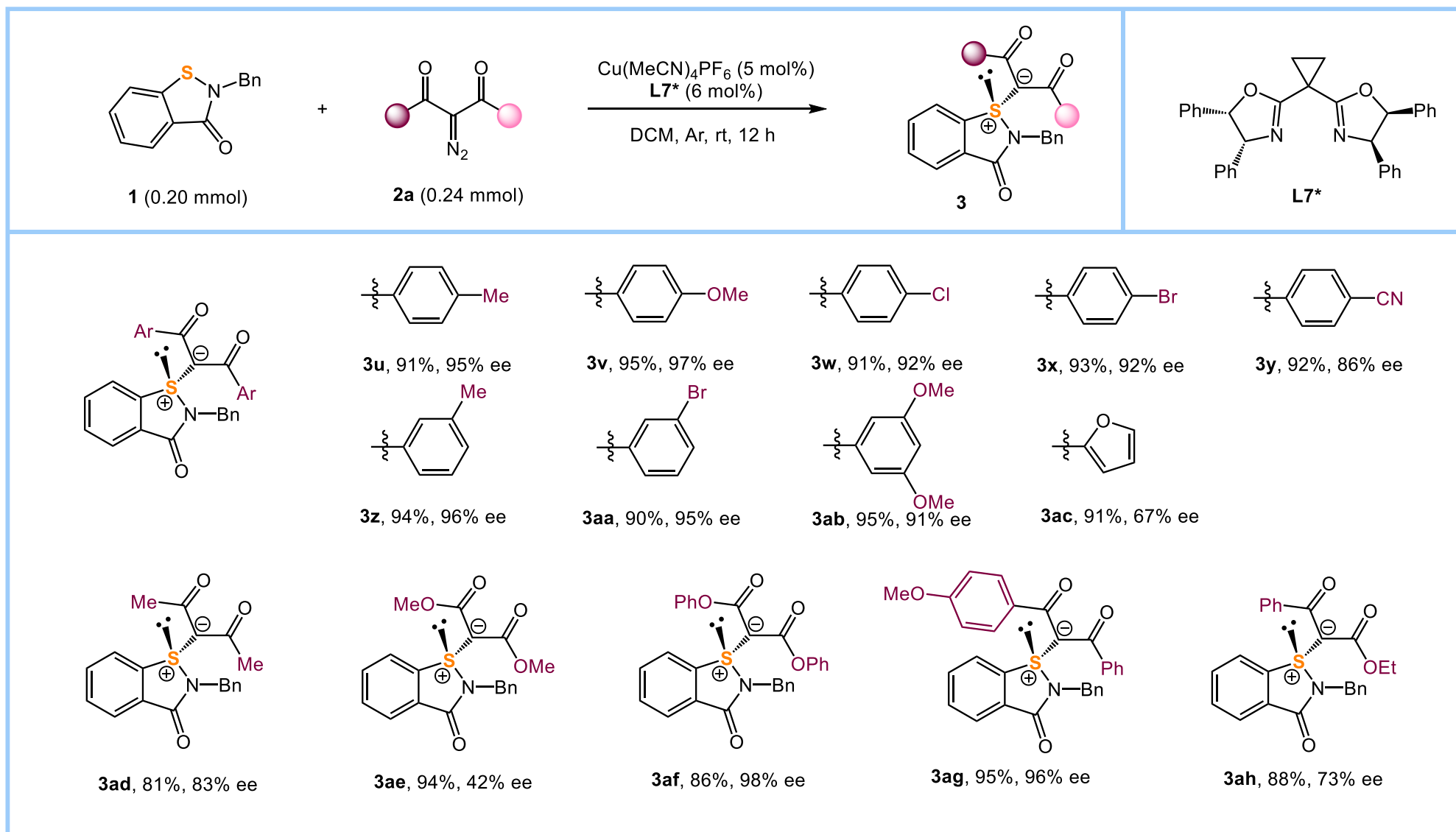
Optimization of Reaction Conditions

Entry	L	X/Y	Solvent	Temp.	Yield (%)	Ee (%)
1	L1	10/12	DCE	40 °C	17	59
2	L2	10/12	DCE	40 °C	5	15
3	L3	10/12	DCE	40 °C	23	2
4	L4	10/12	DCE	40 °C	91	91
5	L5	10/12	DCE	40 °C	81	90
6	L6	10/12	DCE	40 °C	38	73
7	L7	10/12	DCE	40 °C	93	93
8	L7	10/12	DCM	40 °C	93	95
9	L7	10/12	Toluene	40 °C	85	94
10	L7	10/12	THF	40 °C	79	94
11	L7	10/12	EA	40 °C	82	95
12	L7	10/12	DCM	rt	93	95
13	L7	5/6	DCM	rt	93	96

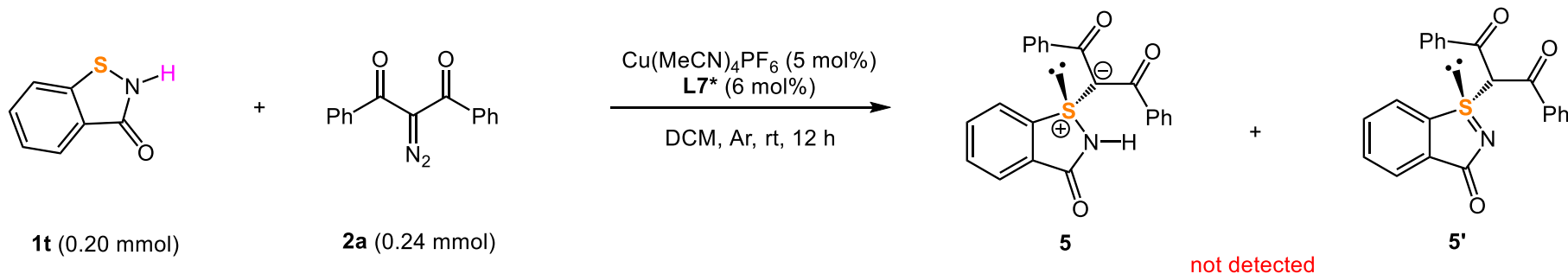
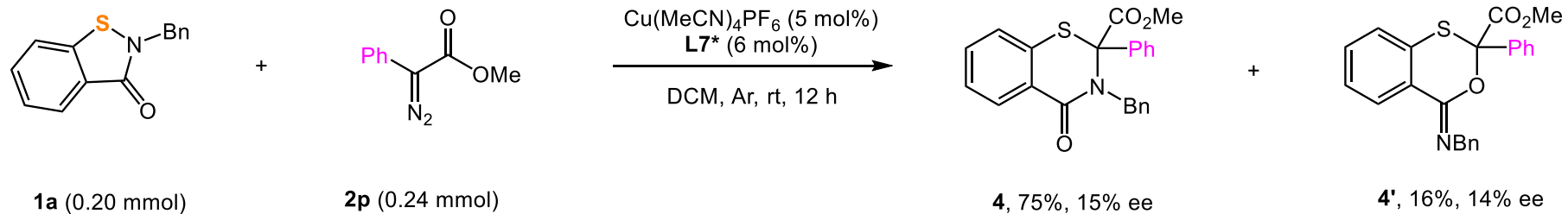
Substrate Scope



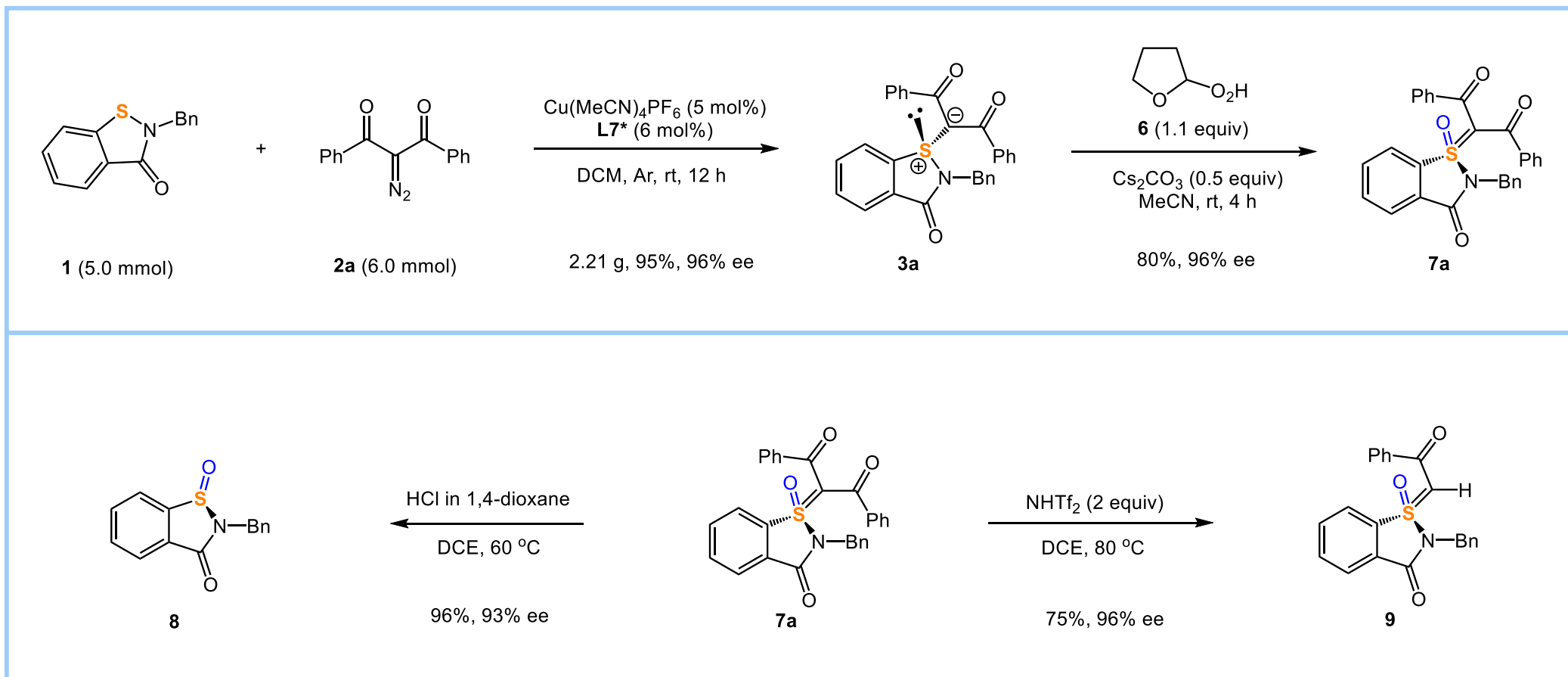
Substrate Scope



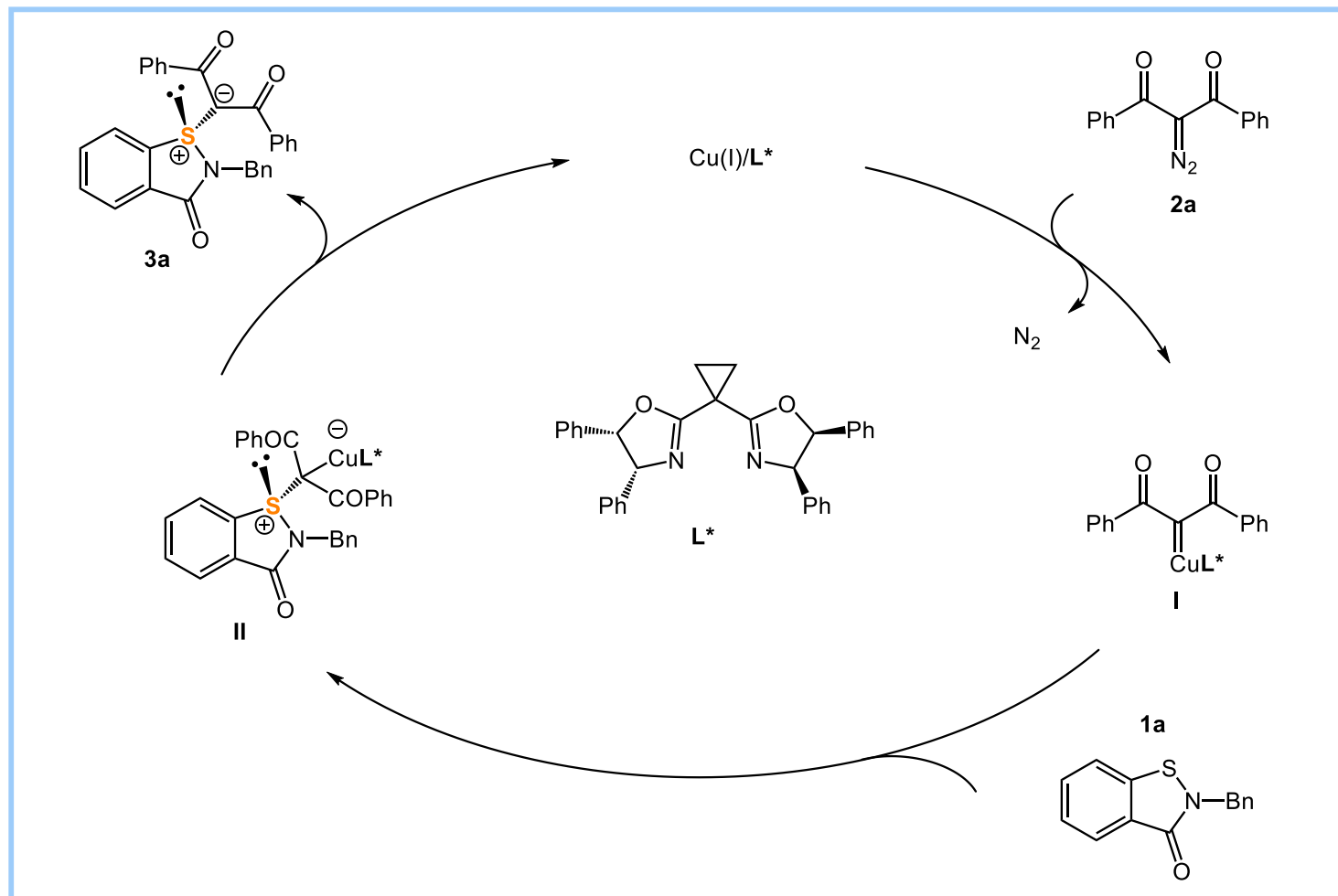
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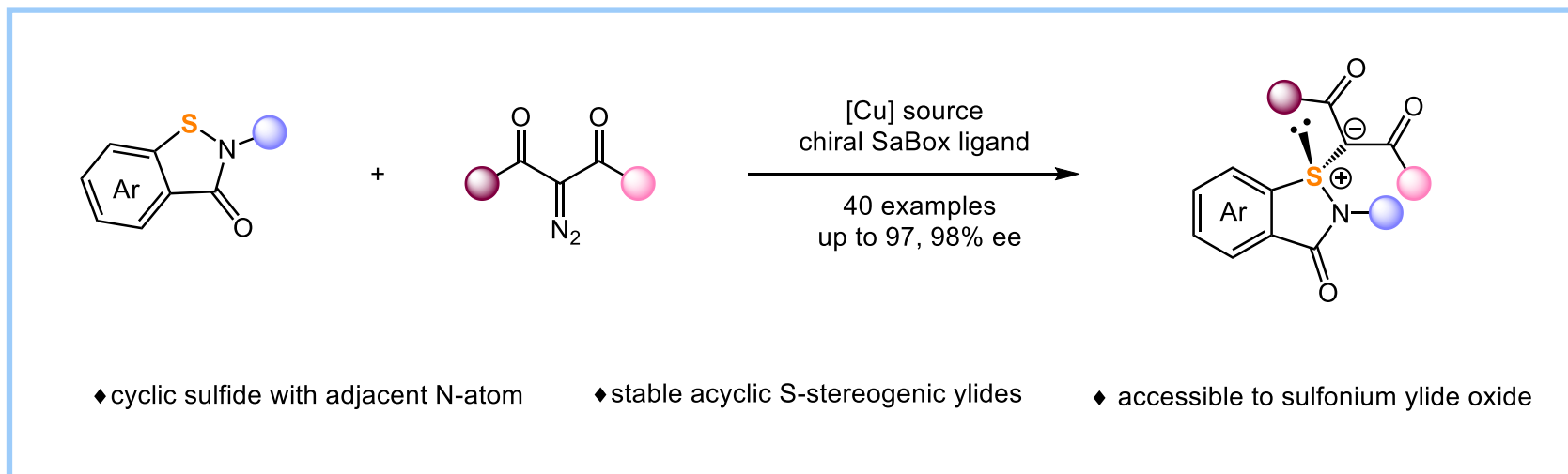
Scale-up Preparation and Transformations



Proposed Mechanism

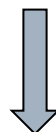


Summary

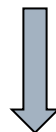


首段写作思路

硫立体中心化合物不对称合成现状



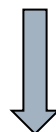
硫手性叶立德作为[2,3]- σ 重排中间体的应用



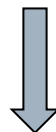
环状稳定硫手性叶立德的成功制备

末段写作思路

实现硫手性氨基硫叶立德的不对称合成



成功关键在于底物的设计以及催化体系的选择



探索稳定硫手性叶立德合成潜力

Representative examples

- ❑ **In sharp contrast**, chiral sulfonium ylides bearing a trigonal pyramidal S-stereogenic center and a carbanion bounded to a positive sulfur have been scarcely reported.. (形成鲜明对比)
- ❑ The development of catalytic asymmetric approaches for constructing configurationally stable structures, particularly those with an intermolecular pattern, **holds great fascination**. (具有极大的吸引力)
- ❑ This hypothesis **was borne out** by the results with B as a representative, although rapid racemization was still observed. (被证实)

Acknowledgment

***Thanks
for your attention !***