

# 螺烯在不对称催化中的应用

报告： 时磊      检查： 段英

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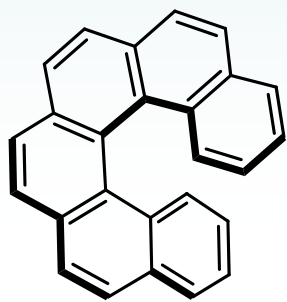
# 1. 简介

随处可见的螺旋手性

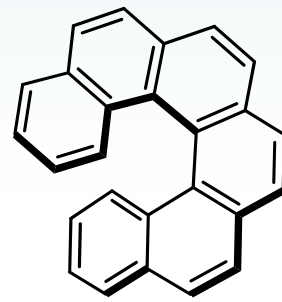


2009年拍摄于梵蒂冈博物馆

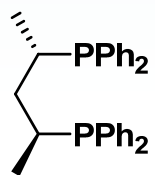
## *Helicene*



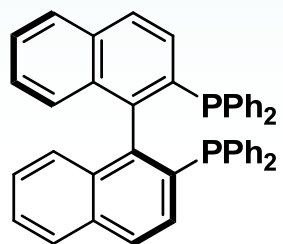
*(M)*-helicity



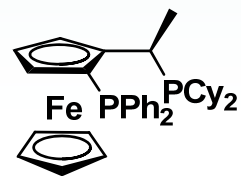
*(P)*-helicity



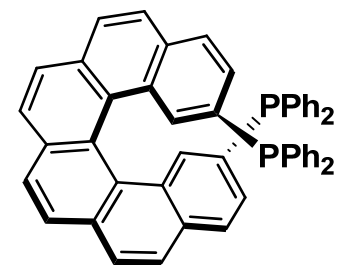
**central chirality**



**axial chirality**



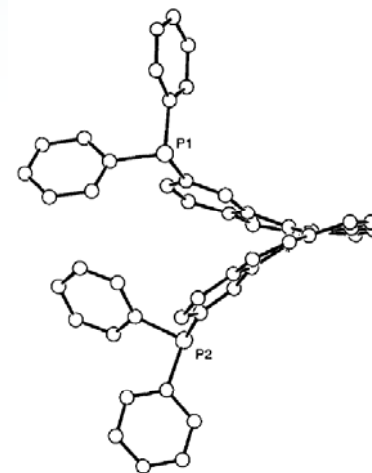
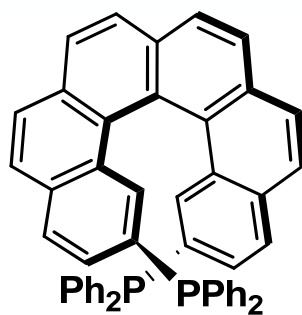
**planar chirality**



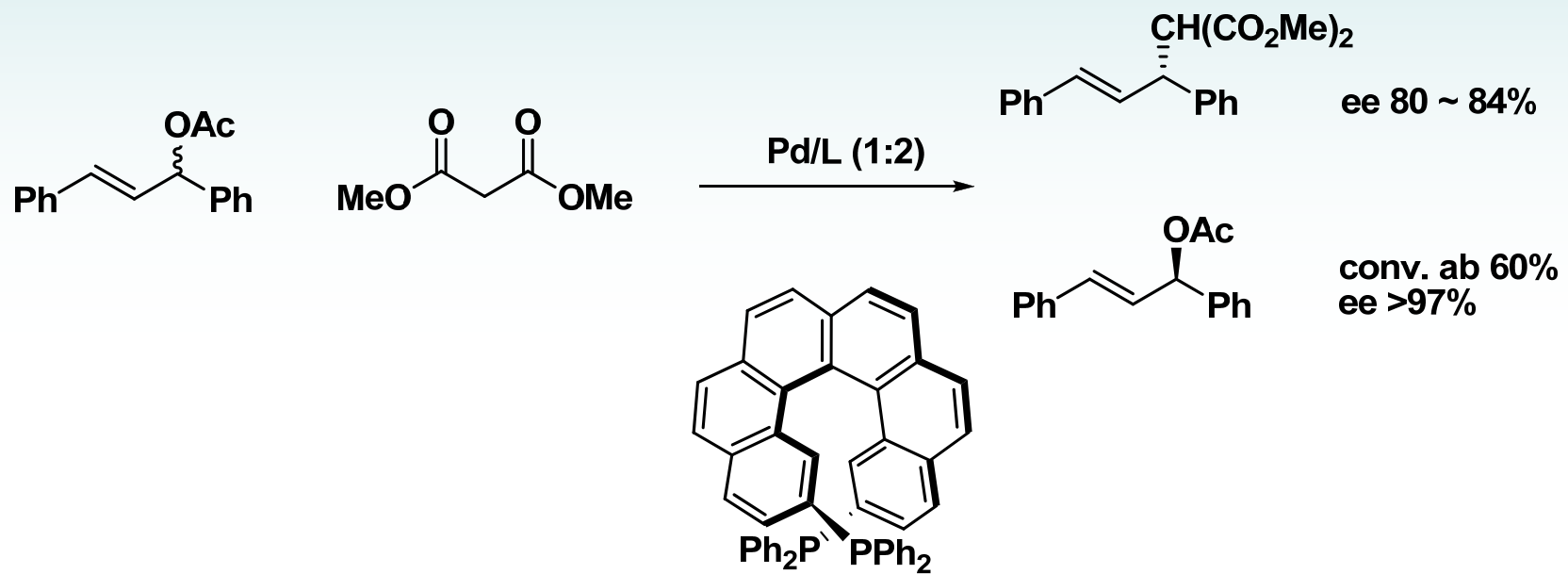
**helical chirality**

## 2. 金属络合物催化剂

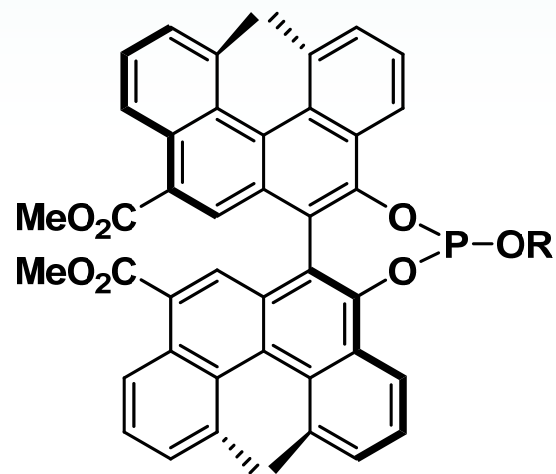
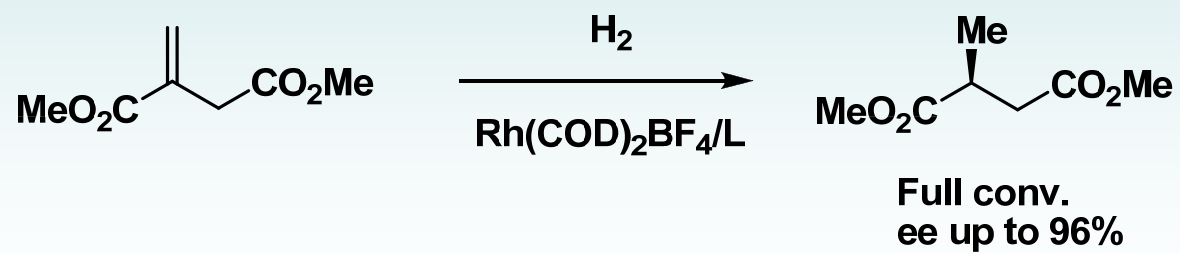
首例报道



Reetz, M. T. *et al. Tetrahedron Lett.* **1997**, 38, 3211.



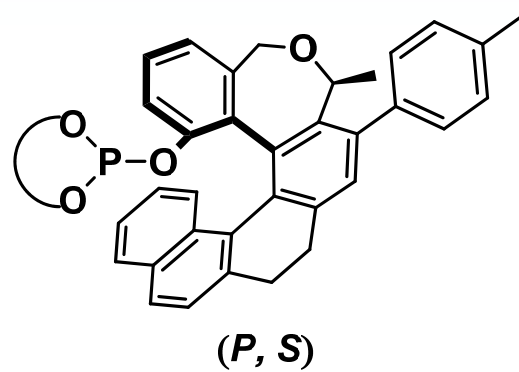
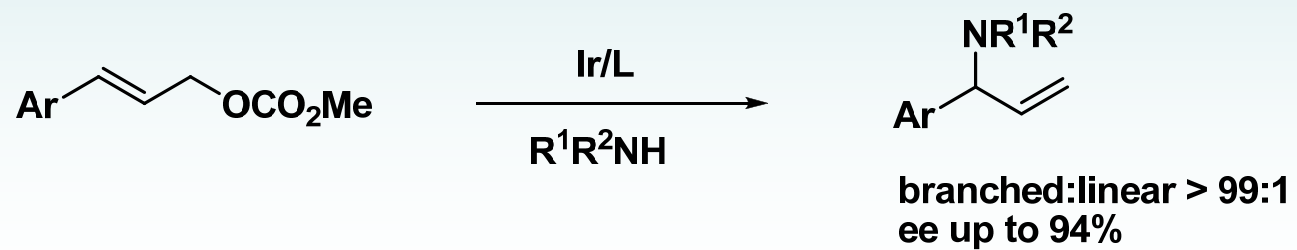
Reetz, M. T. *et al.* *J. Organomet. Chem.* **2000**, 603, 105.



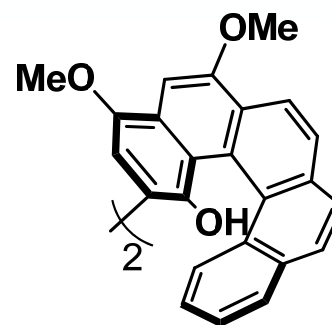
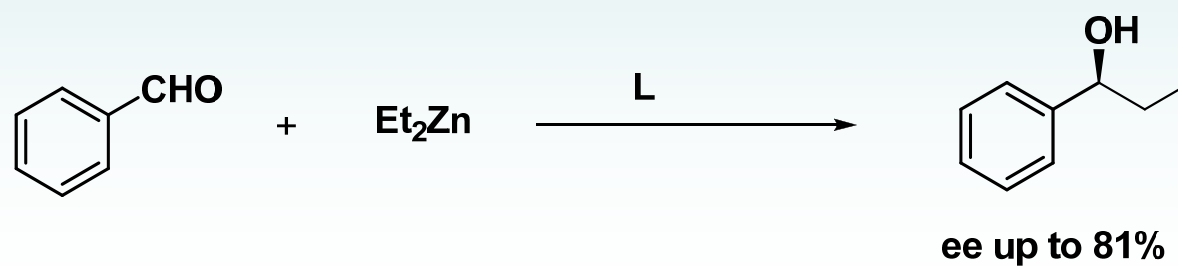
*(M, M, S, I)* R = menthyl

Yamaguchi, M. *et al.* *Tetrahedron Lett.* **2003**, *44*, 4969.



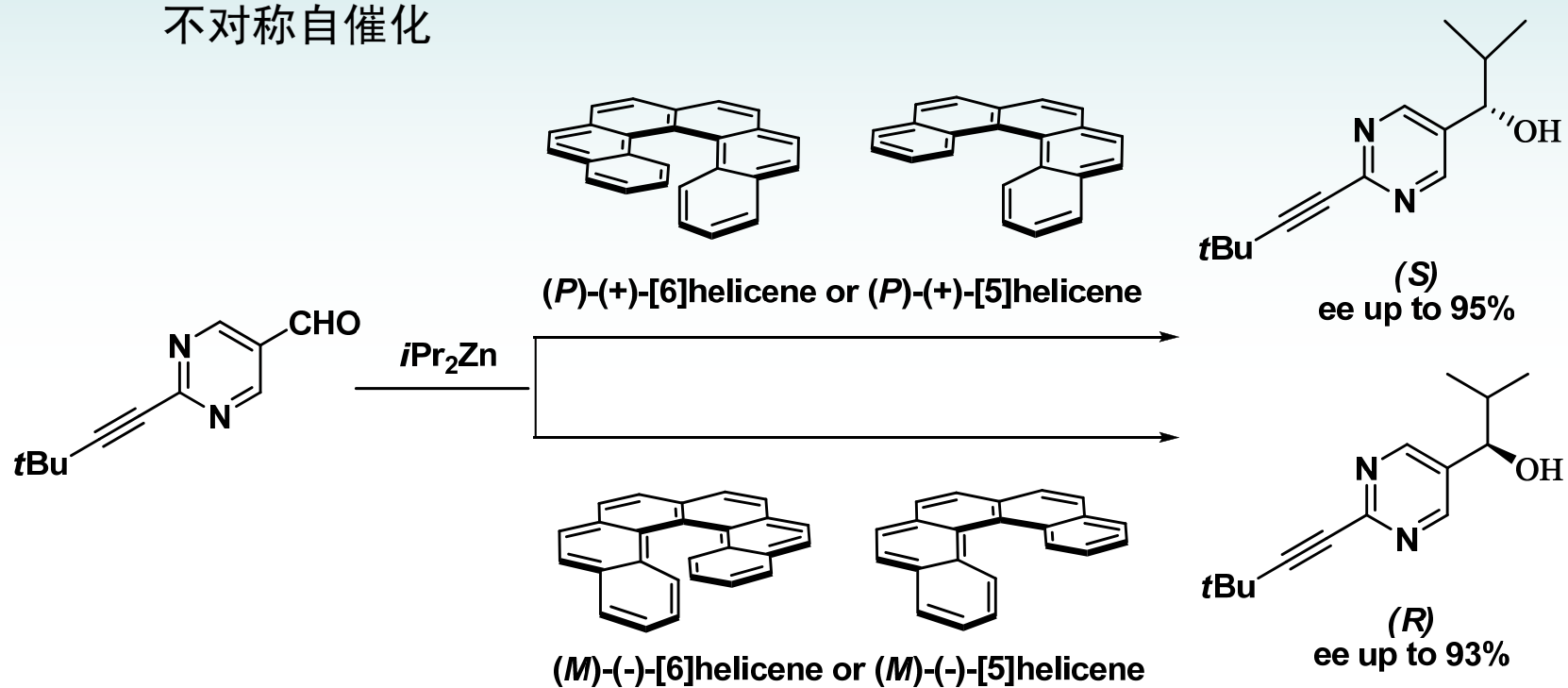


Starý, I. *et al. Eur. J. Org. Chem.* **2011**, 3849.

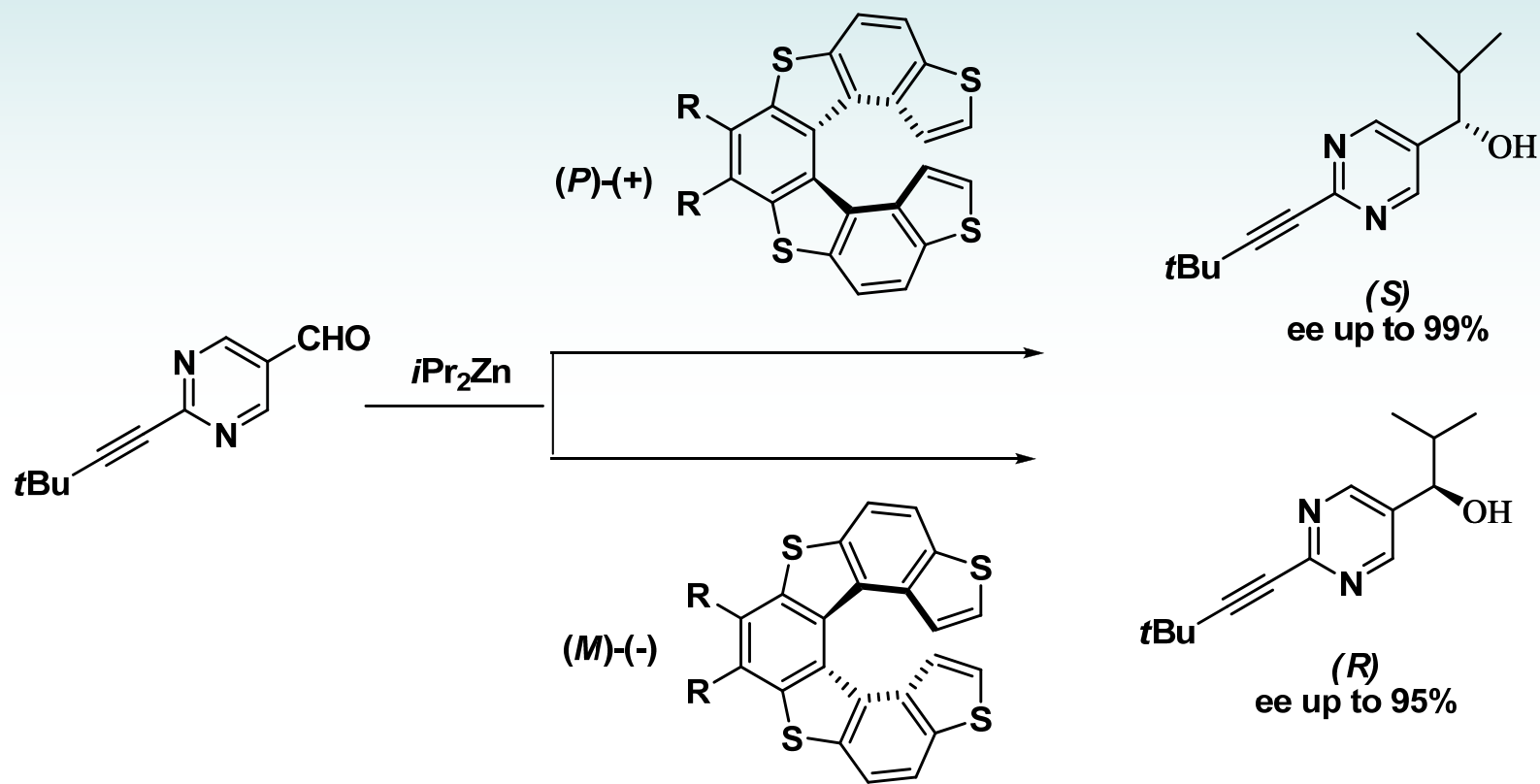


Katz, T. J. *et al.* *J. Org. Chem.* **2000**, 65, 815.

# 不对称自催化

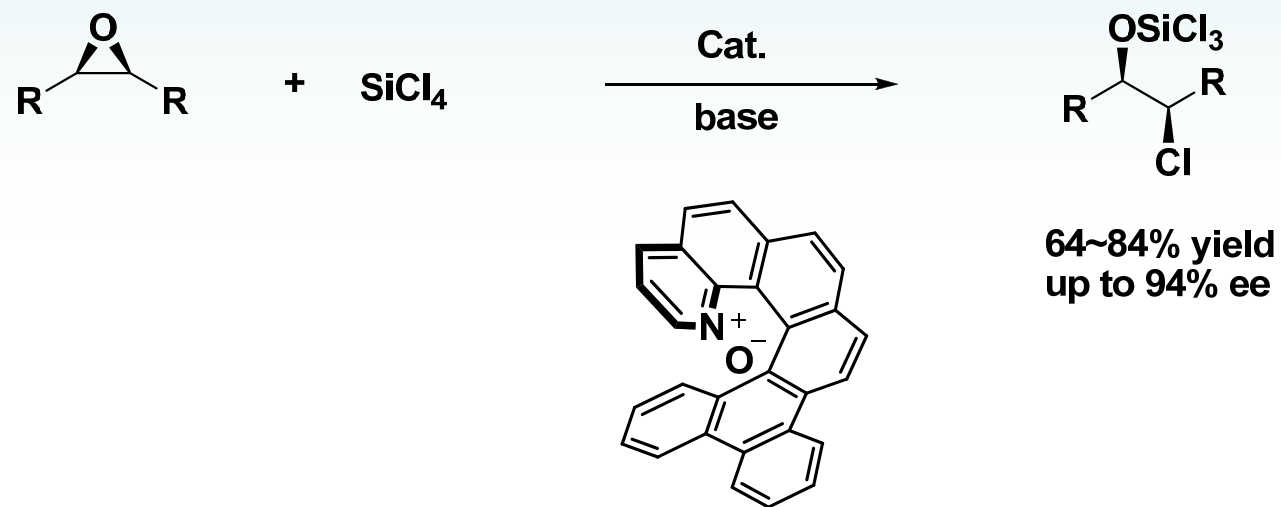


Soai, K. et al. *Angew. Chem. Int. Ed.* **2005**, *44*, 6700.

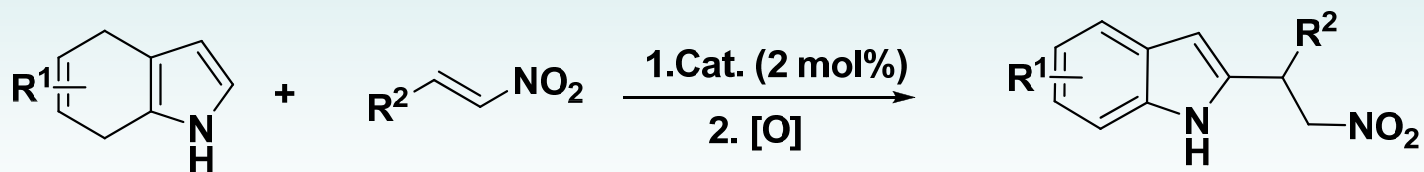


Soai, K. *et al. Tetrahedron: Asymmetry* **2006**, *17*, 2050.

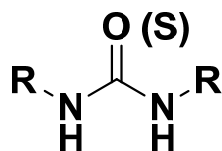
### 3. 有机小分子催化剂



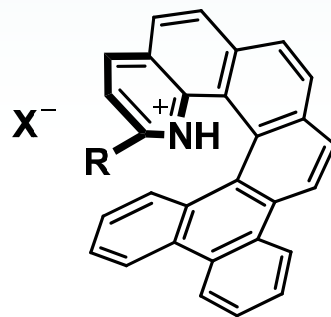
Takenaka, N. *et al. Angew. Chem. Int. Ed.* **2005**, 44, 6700.



up to 90% yield  
 up to 96% ee



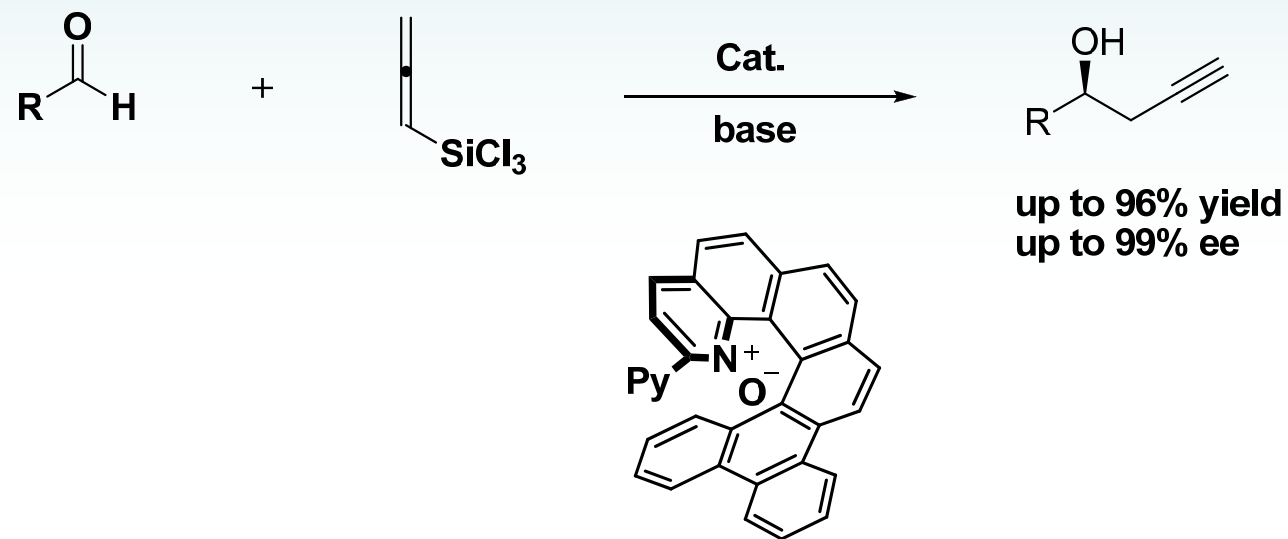
pKa = ca. 27(21) in DMSO



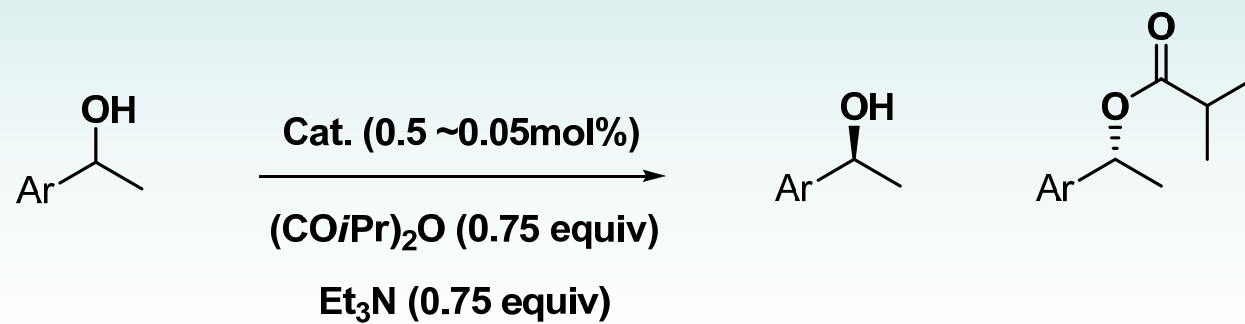
R = 1-adNH

pKa = ca. 6 in DMSO

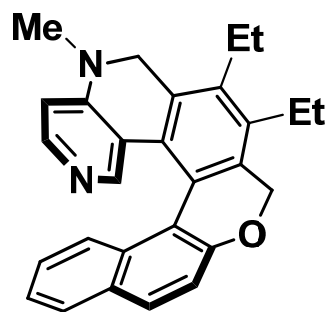
Takenaka, N. *et al. J. Am. Chem. Soc.* **2010**, *132*, 4536.



Takenaka, N. *et al. Org. Lett.* **2011**, *13*, 1654.



s up to 116



Carbery, D. R. et al. *Org. Lett.* **2011**, *13*, 1250.



## 总结与展望

- 缺点：合成困难；不易修饰；溶解性较差。
- 优点：性质稳定，用量小，可回收。

设计基于螺烯的金属和有机小分子催化剂

新的设计思想

$\pi$ - $\pi$  stacking

光催化

新大陆？



## 参考文献

- 1) Reetz, M. T. *et al. Tetrahedron Lett.* **1997**, 38, 3211.
- 2) Reetz, M. T. *et al. J. Organomet. Chem.* **2000**, 603, 105.
- 3) Yamaguchi, M. *et al. Tetrahedron Lett.* **2003**, 44, 4969.
- 4) Soai, K. *et al. Angew. Chem. Int. Ed.* **2005**, 44, 6700.
- 5) Soai, K. *et al. Tetrahedron: Asymmetry* **2006**, 17, 2050.
- 6) Starý, I. *et al. Eur. J. Org. Chem.* **2011**, 3849.
- 7) Katz, T. J. *et al. J. Org. Chem.* **2000**, 65, 815.
- 8) Takenaka, N. *et al. Angew. Chem. Int. Ed.* **2005**, 44, 6700.
- 9) Takenaka, N. *et al. J. Am. Chem. Soc.* **2010**, 132, 4536.
- 10) Takenaka, N. *et al. Org. Lett.* **2011**, 13, 1654.
- 11) Carbery, D. R. *et al. Org. Lett.* **2011**, 13, 1250.
- 12) Chen, C.-F. *et al. Chem. Rev.* **2012**, 112, 1463.

水平有限，欢迎批评指正！

