

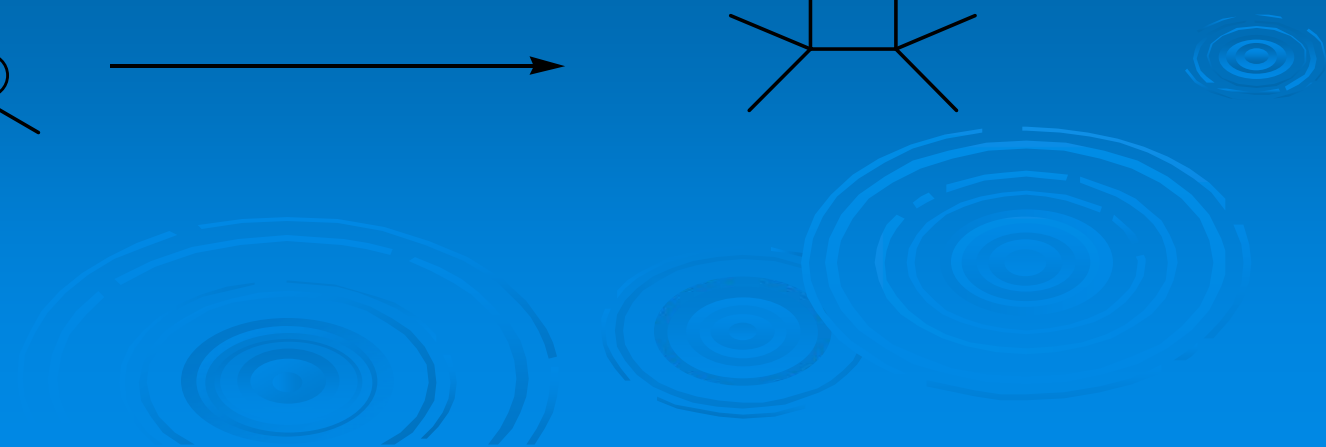
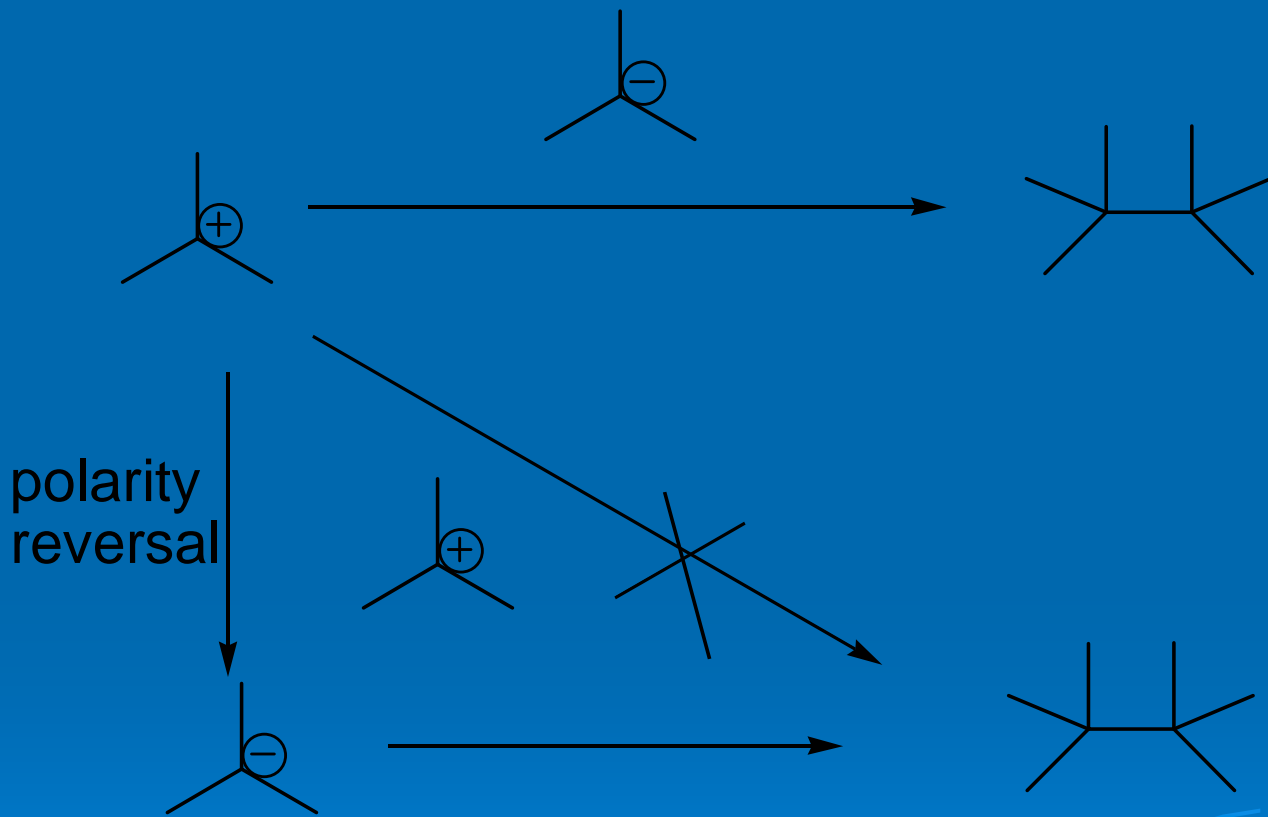
极性反转有机小分子催化剂 催化的反应——*NHC*

Reactions Catalyzed by Polarity Reversal
(Reactivity Umpolung) Organocatalyst

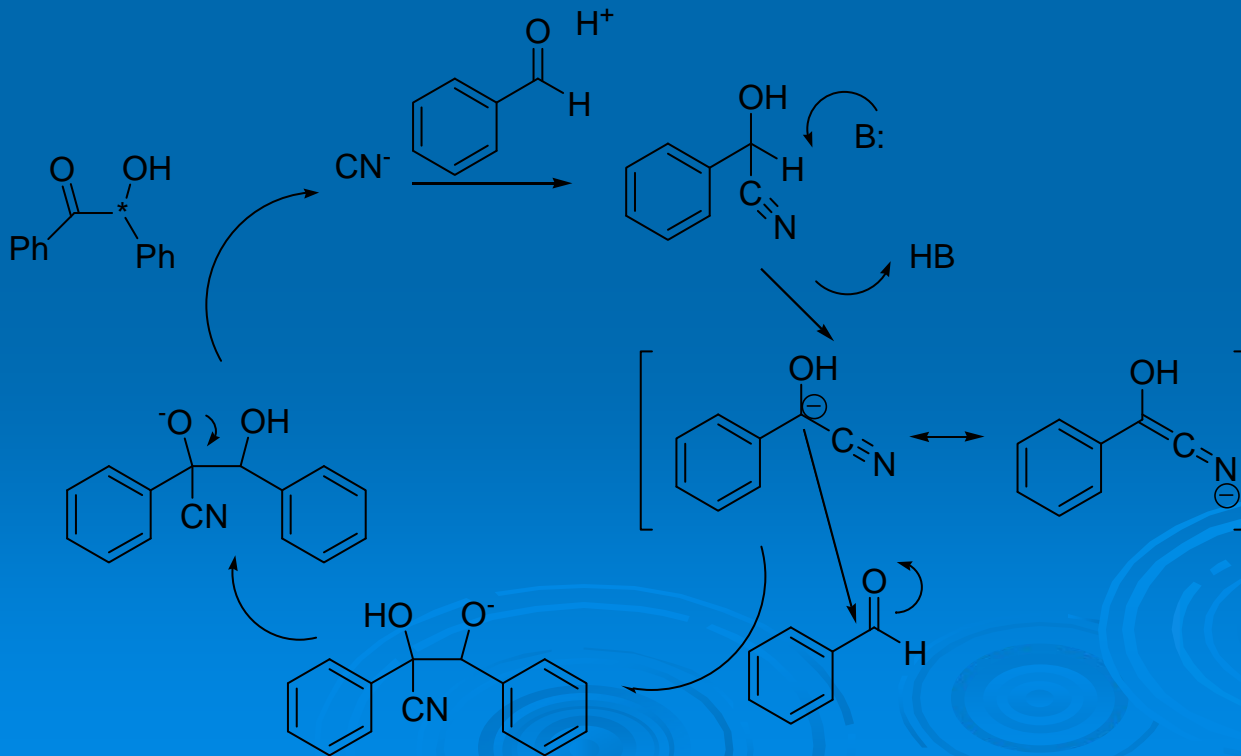
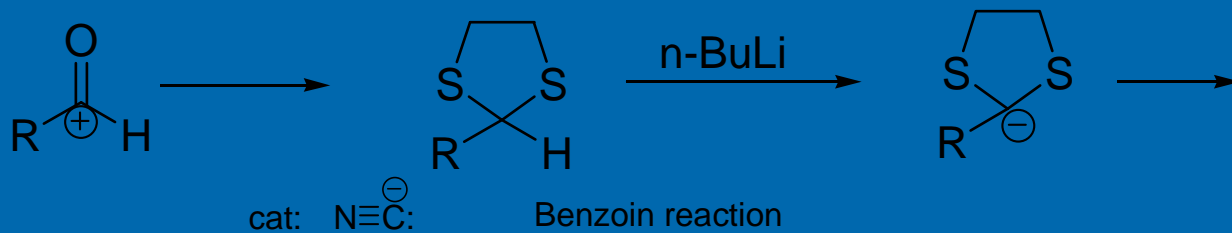
-----*NHC*

Guoqiang Yang

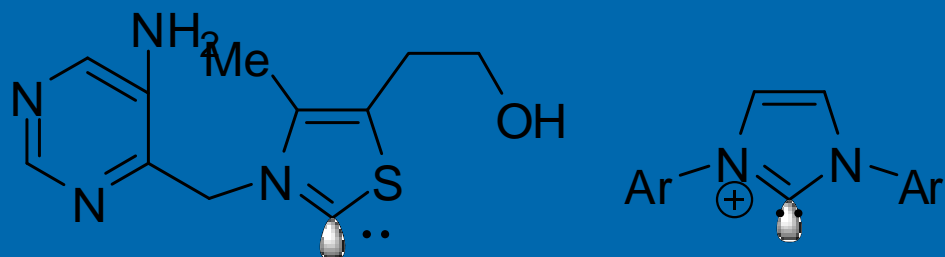
07, 09, 29



极性反转试剂

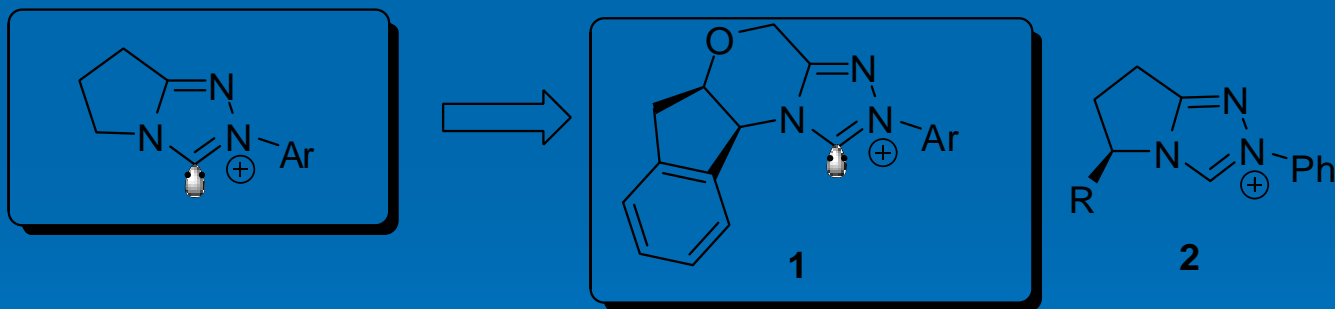


N-Heterocyclic Carbene Catalysis

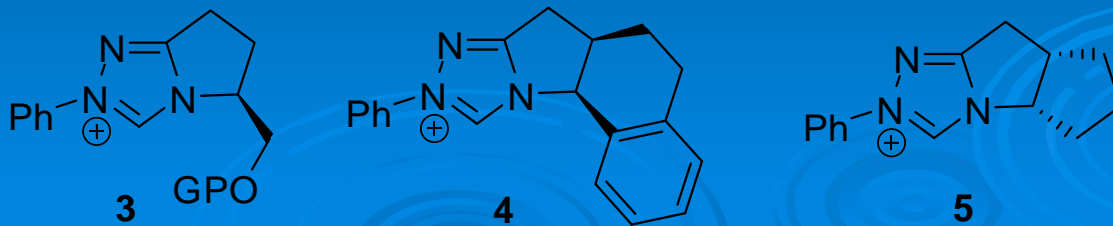


VB₁ thiazolium

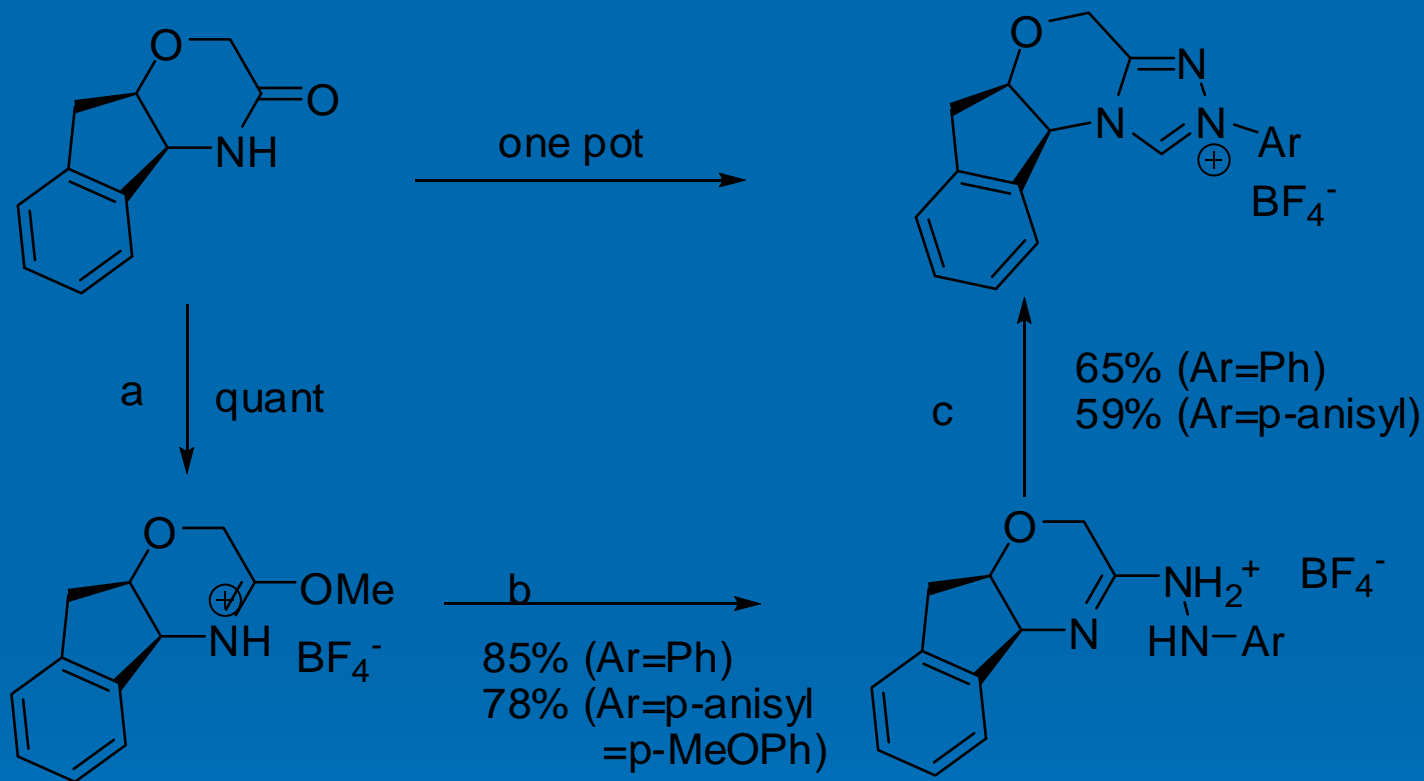
三唑系列 triazolium



Got the best results in many reactions



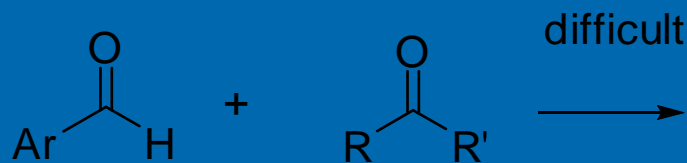
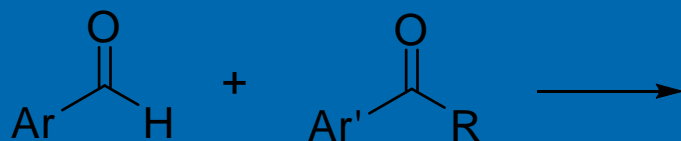
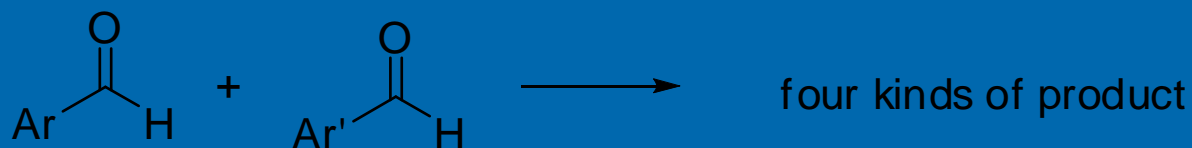
The Synthesis of catalyst **1**



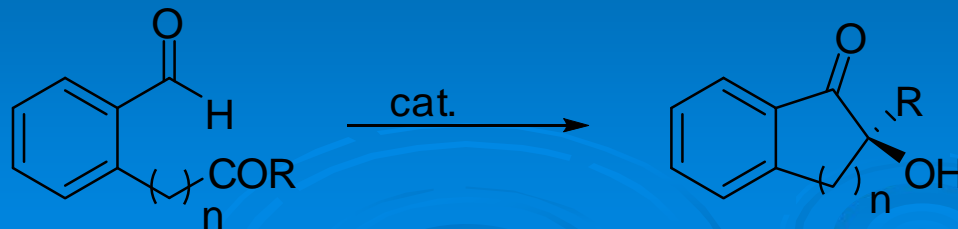
(a) $\text{Me}_3\text{O}^+\text{BF}_4^-$, CH_2Cl_2 , 23°C , 12h; (b) phenylhydrazine or p-anisylhydrazine, 23°C , 30min; (c) PhCl , $\text{HC}(\text{OEt})_3$, 110°C , 12h

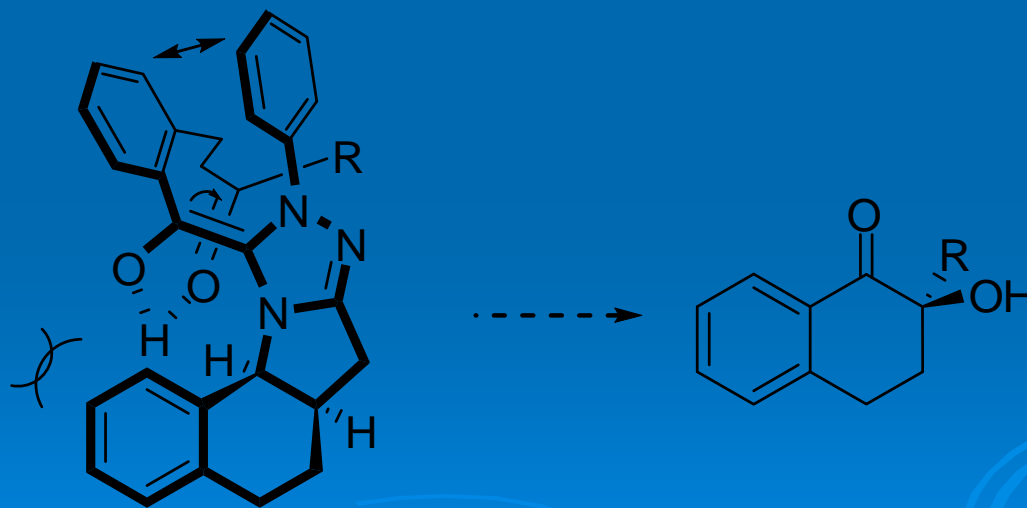
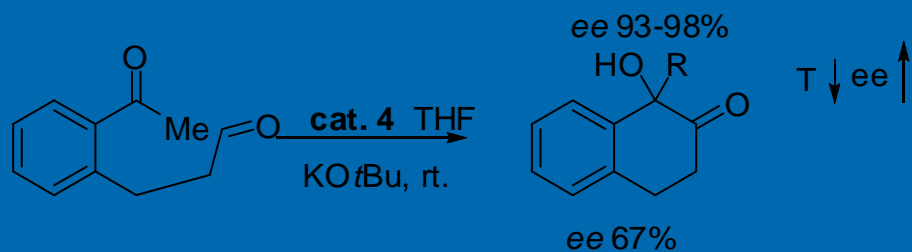
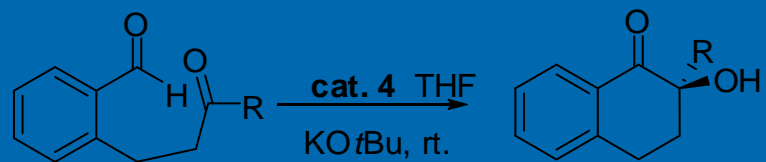
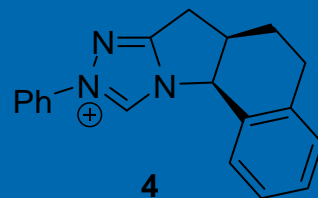
1) Rovis, T. *et al.*, *J. Org. Chem.* **2005**, *70*, 5725-5728

1. Intramolecular Crossed-Benzoin Reactions



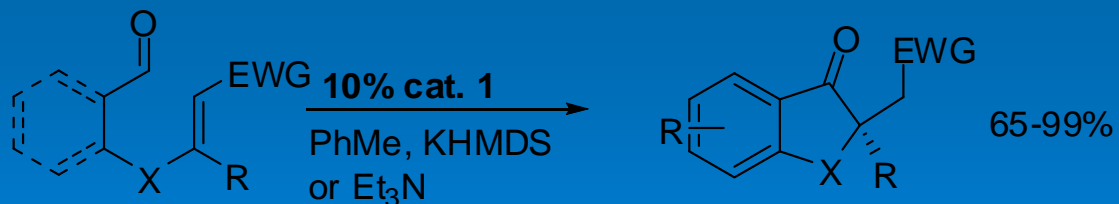
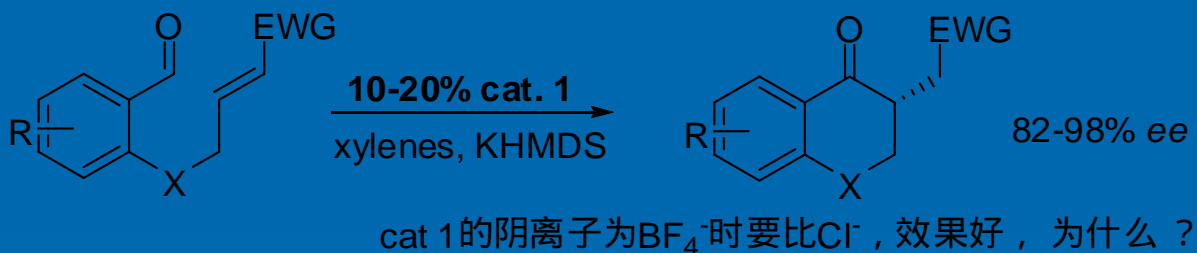
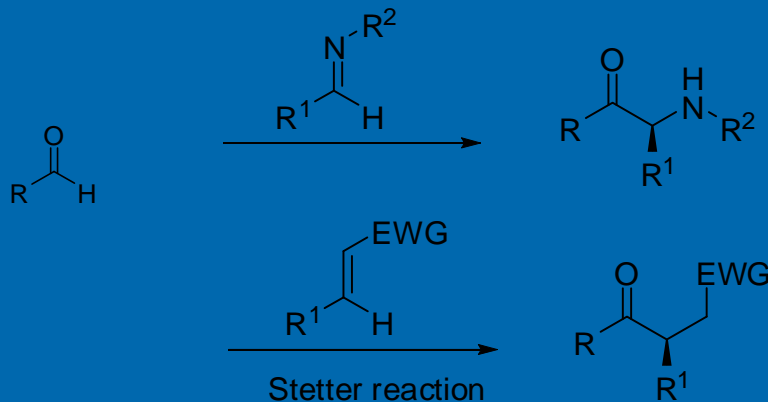
How?



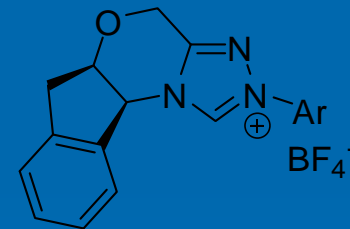


2) Enders, D. *et al.*, *Angew. Chem. Int. Ed.* **2006**, *45*, 1463-1467

2. 同样的机理还可做什么底物？



X = O, NR, S, CH_2

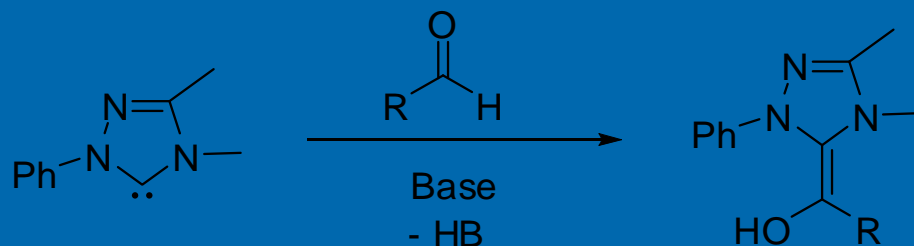


3) Rovis, T. *et al.*, *J. Am. Chem. Soc.* **2002**, 124, 10298-10299

4) Rovis, T. *et al.*, *J. Am. Chem. Soc.* **2004**, 126, 8876-8877

3. 如何衍生反应!

➤ 分析1:



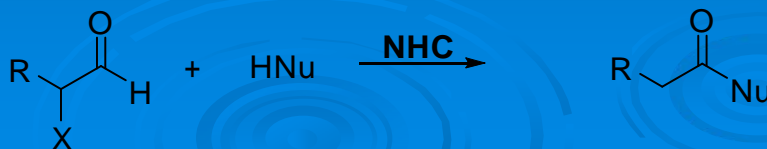
学习Stetter reaction
利用共轭

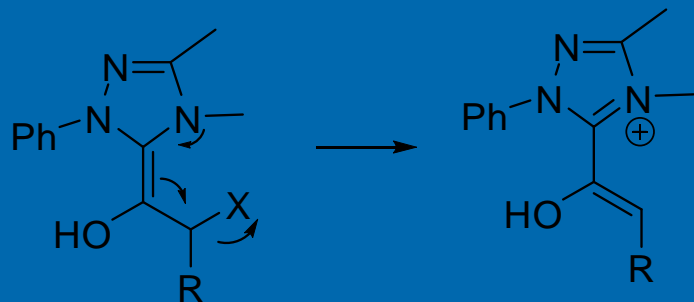


Nu= HOR (酚, 醇等)

5) Rovis, T. *et al.*,
J. Am. Chem. Soc.
2004, 126, 9518-9519

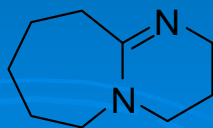
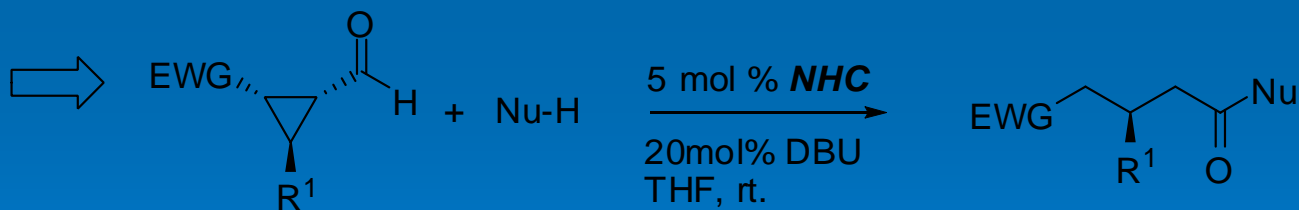
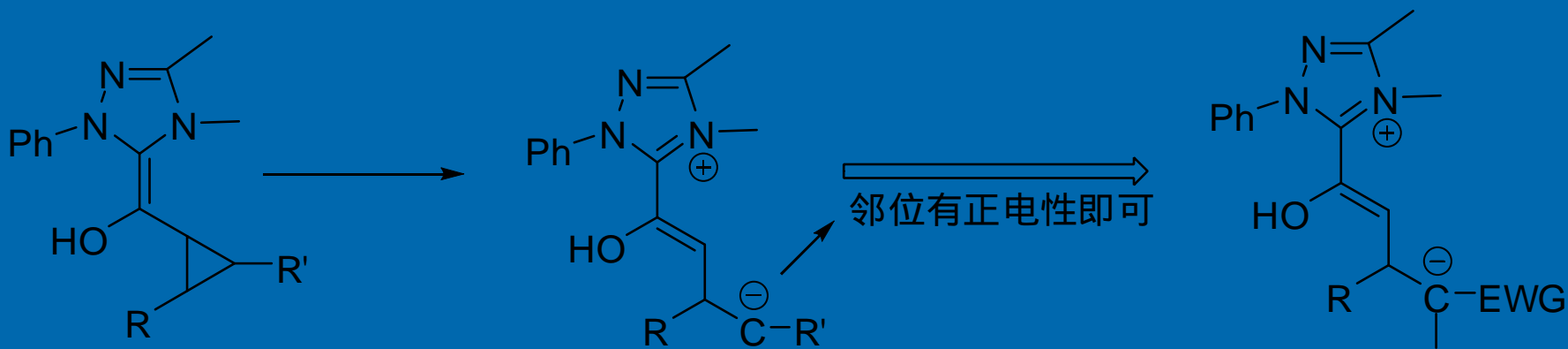
所得反应:





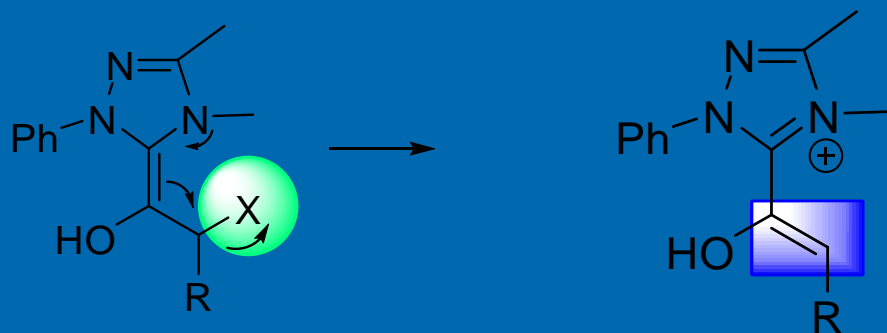
X=O, N 可以，那么C是否可以？

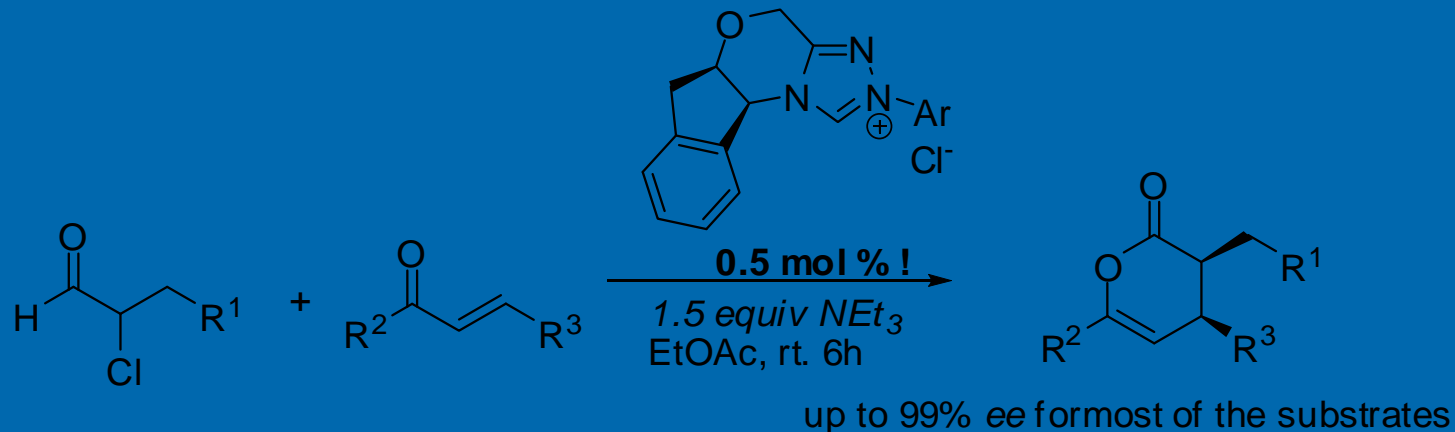
➤ 分析3: 只要使离去后的产物稳定即可，那么如何使之稳定？



1,8-Diazabicyclo[5,4,0]-undec-7-ene

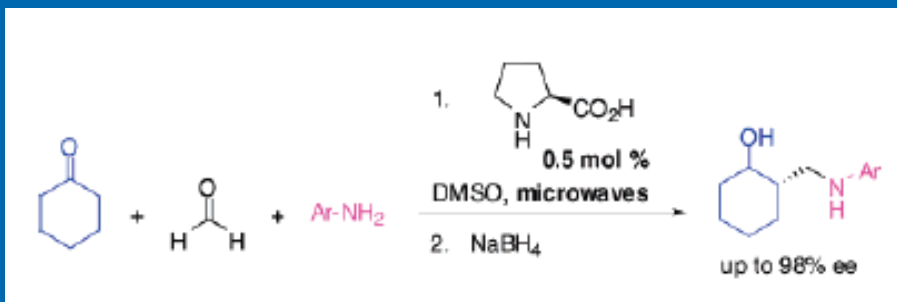
4. 逆回去想问题， 还有出路!





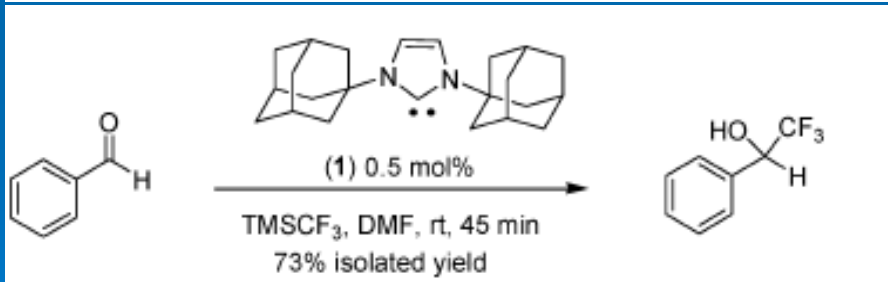
8) Bode, J. W. *et al.*, *J. Am. Chem. Soc.* **2006**, *128*, 15088-15089

b



(b) Cat: DHQD-PEN

c



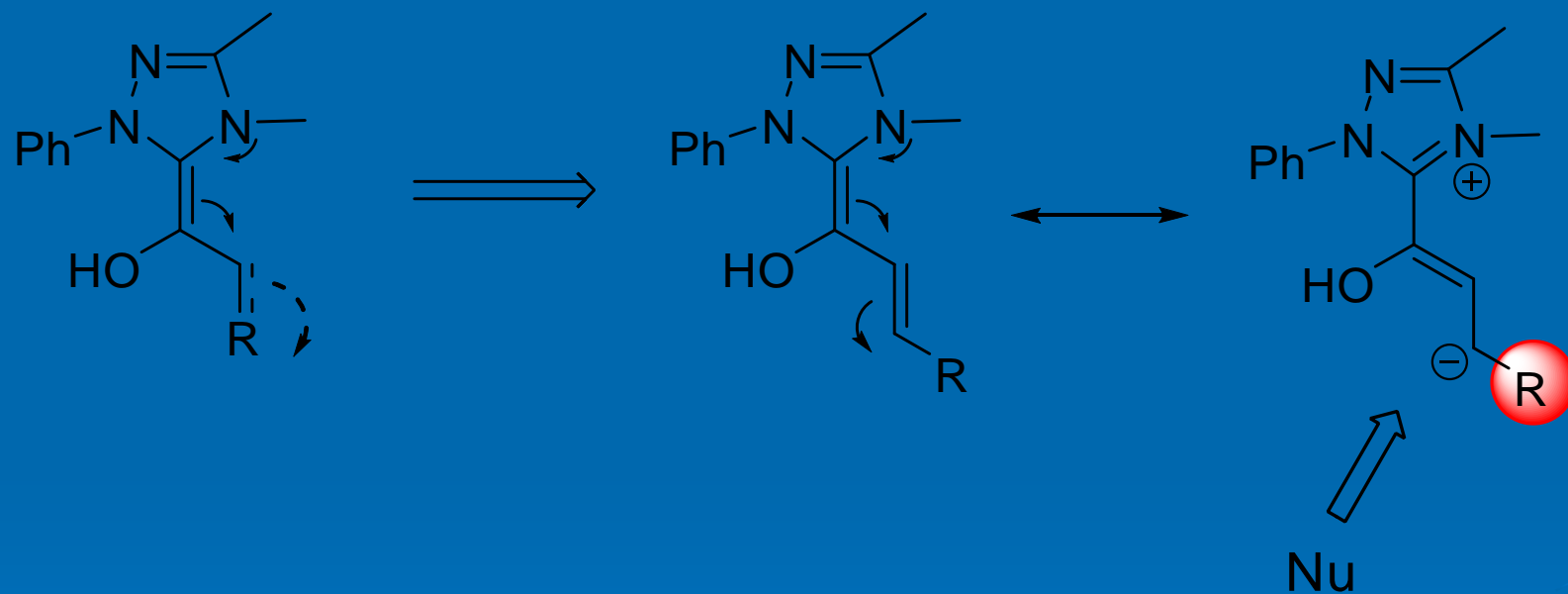
Michael Addition Reaction

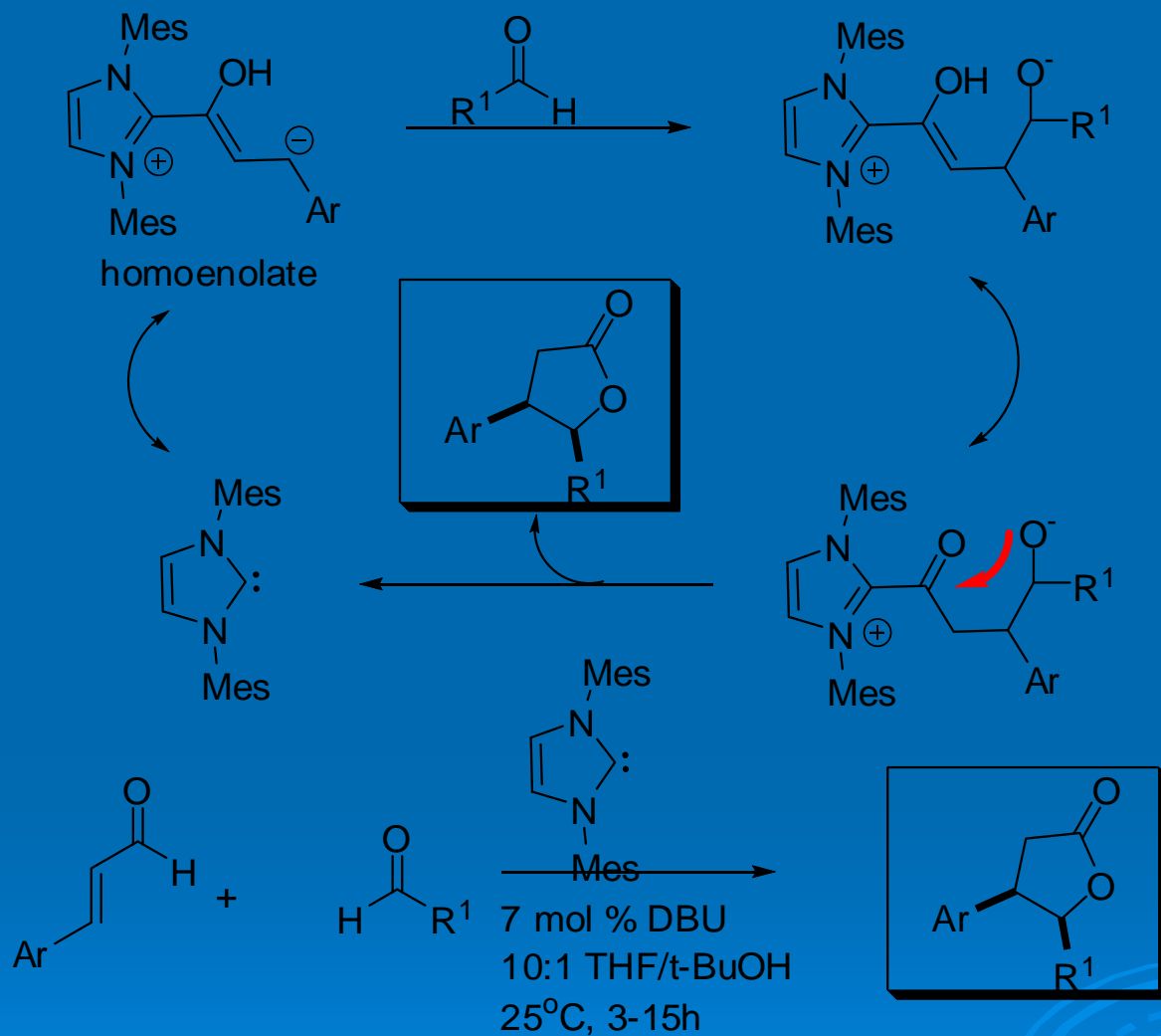
9) (a) Wu, F. *et al.*, *angew. Chem. Int. Ed.* **2006**, *45*, 4301-4305;

(b) Bolm, C. *et al.*, *J. Org. Chem.* **2006**, *71*, 2888-2891;

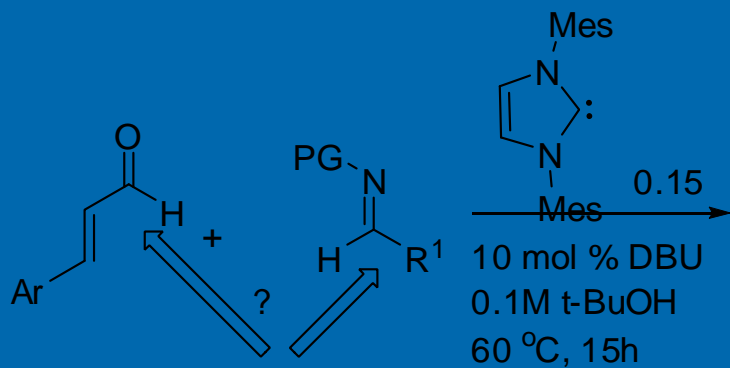
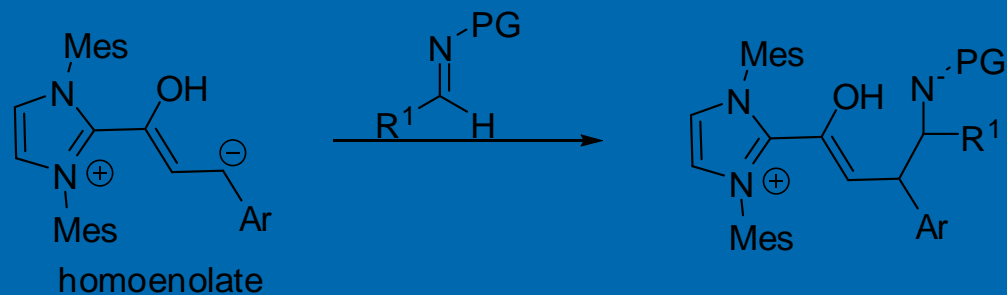
(c) Song, J. J. *et al.*, *Org. Lett.* **2005**, *7*, 2193-5196

再逆回去想问题，还有出路!

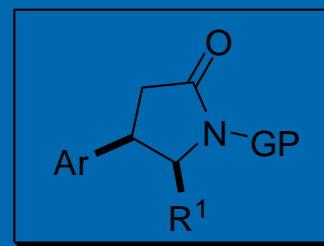




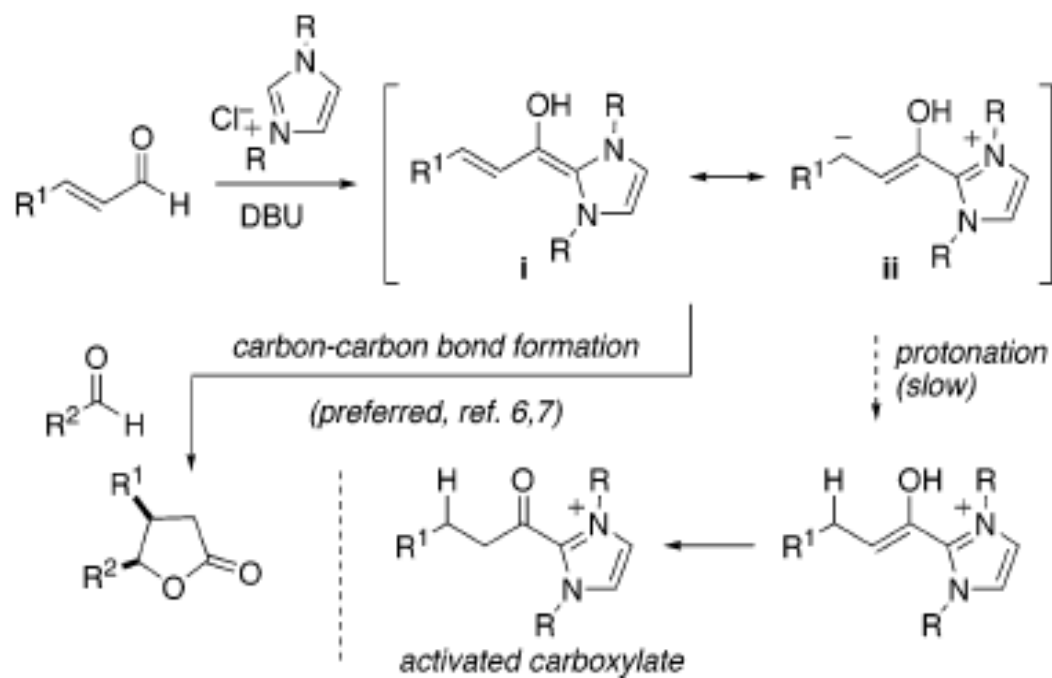
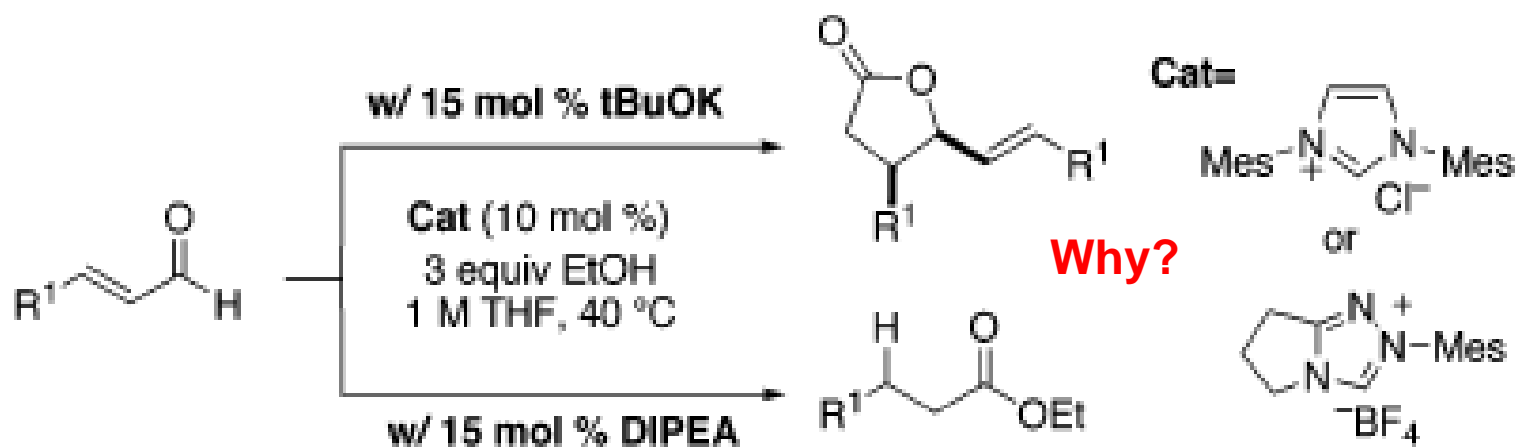
10) Bode, J. W. *et al.*, *J. Am. Chem. Soc.* **2004**, *126*, 14370-14371



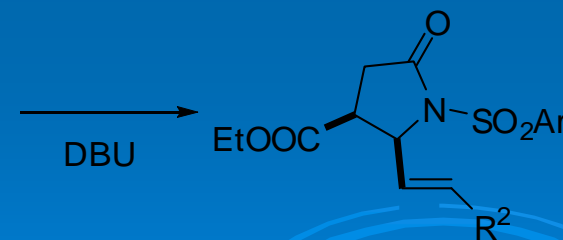
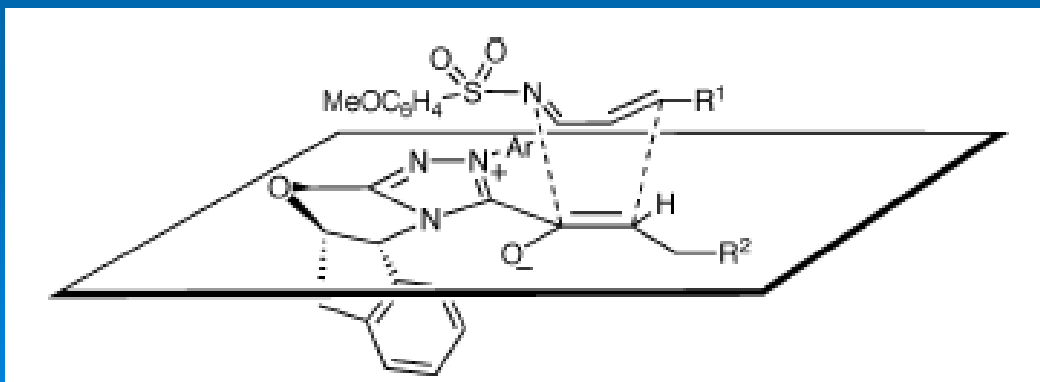
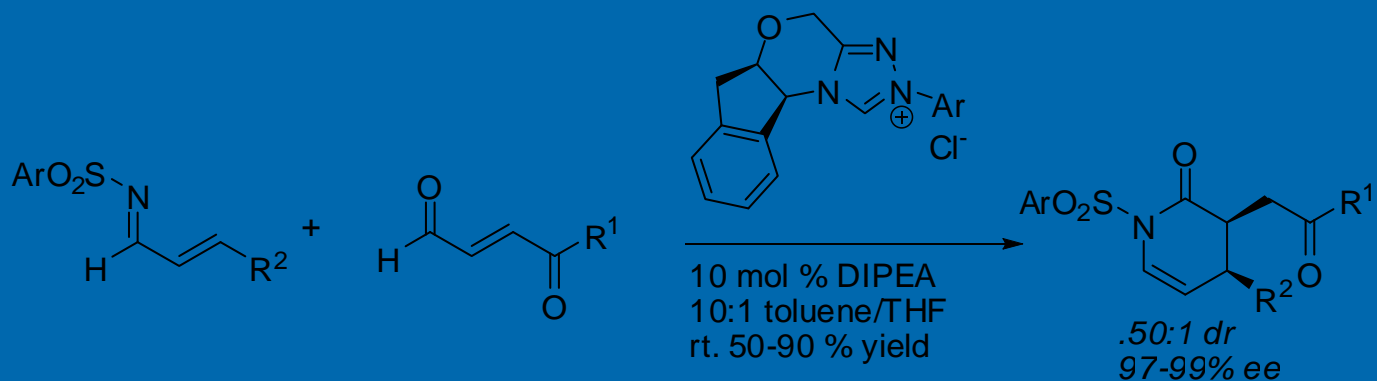
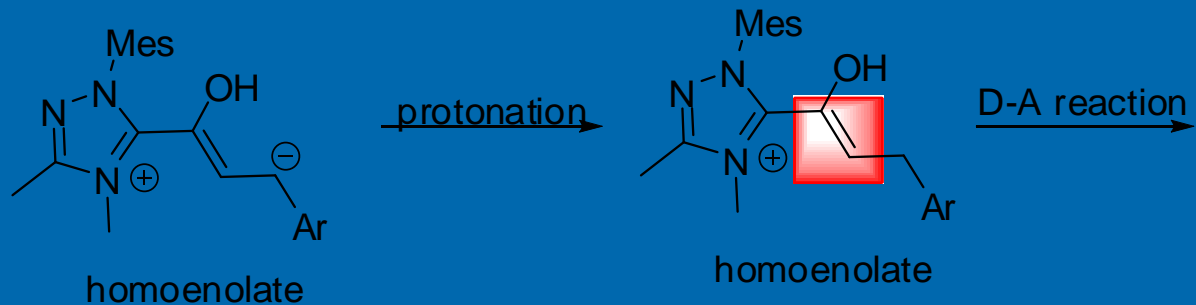
what kind of PG?

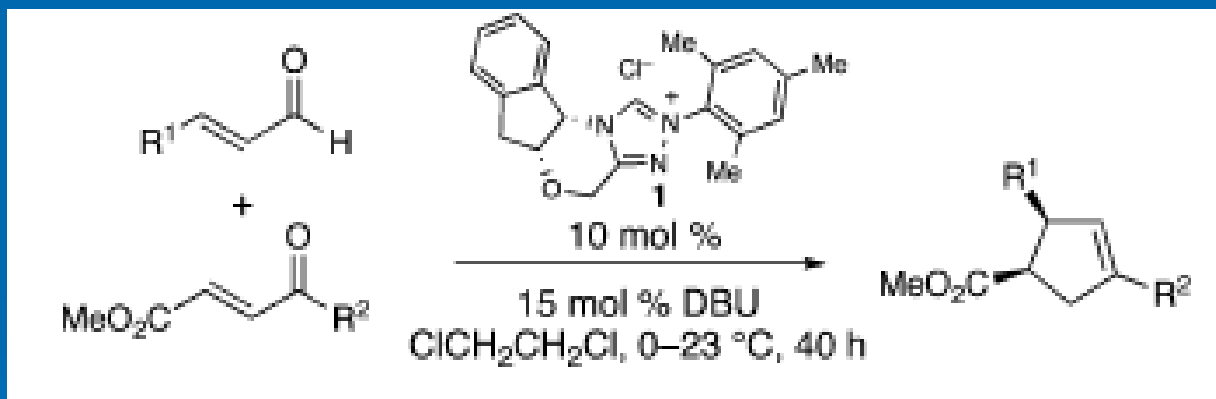
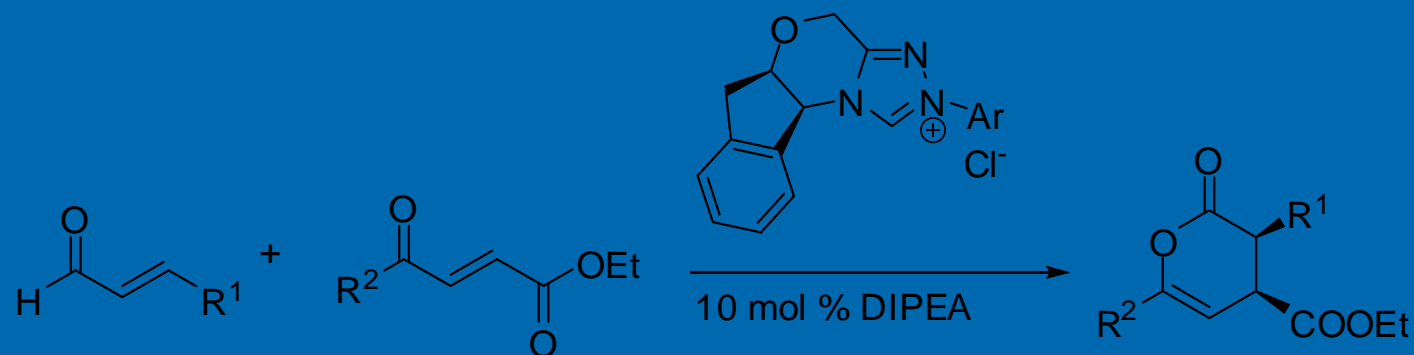


11) Bode, J. W. *et al.*, *Org. Lett.* **2005**, 7, 3131-3134

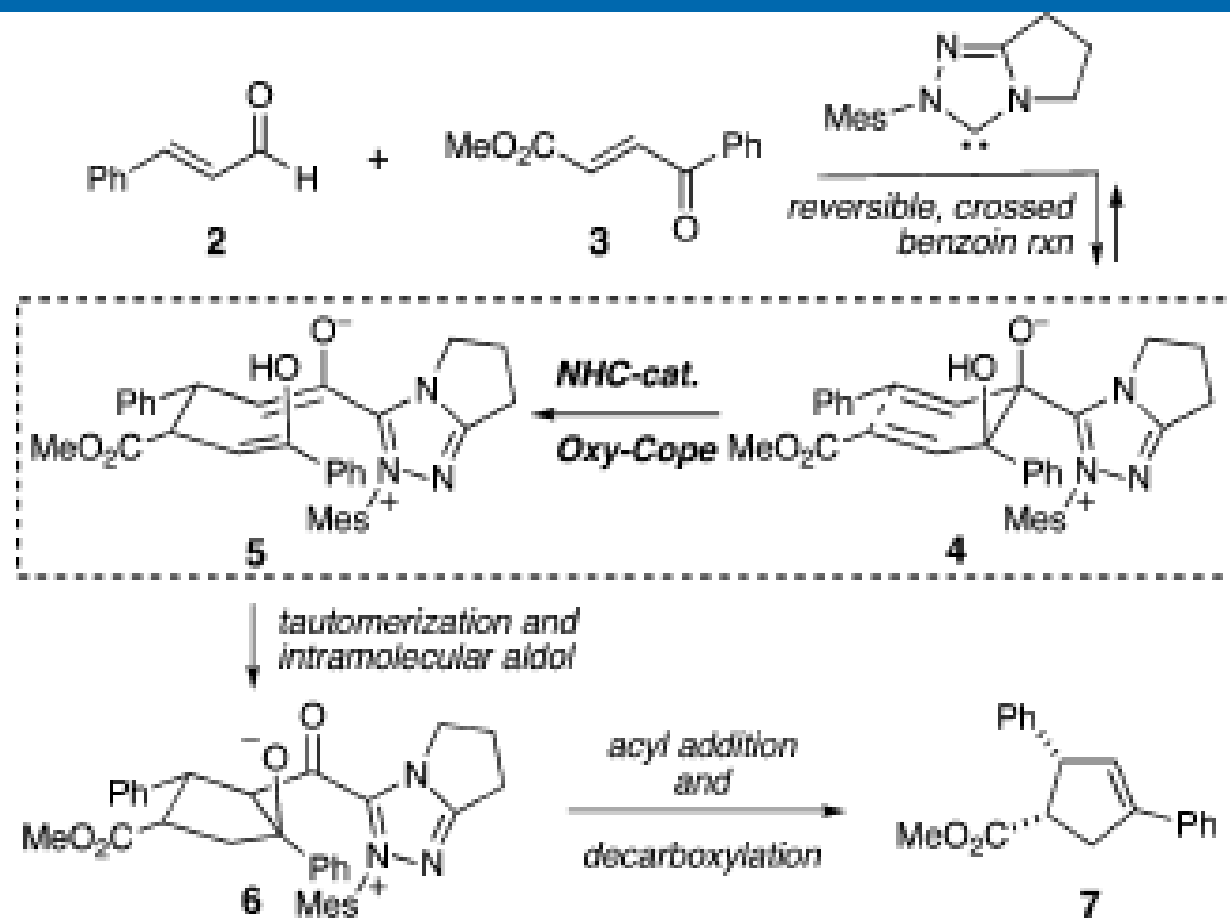


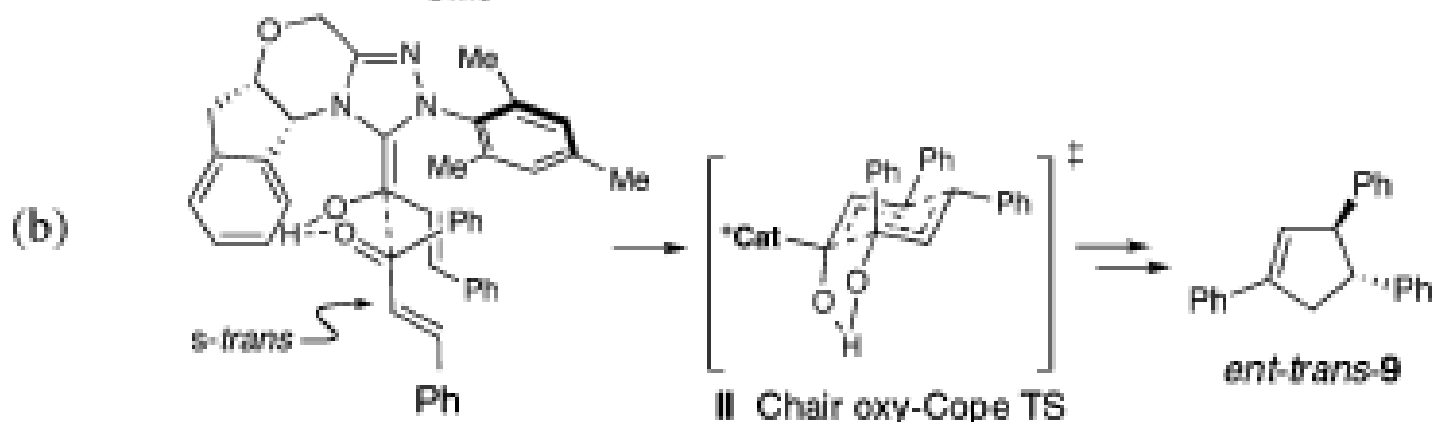
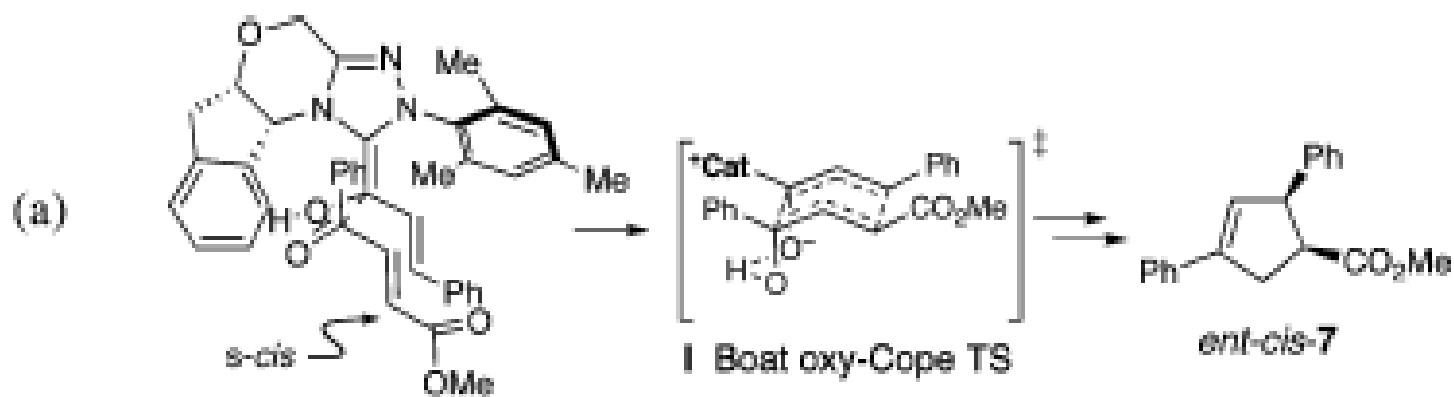
12) Bode, J. W. *et al.*, *Org. Lett.* 2005, 7, 3873-3876



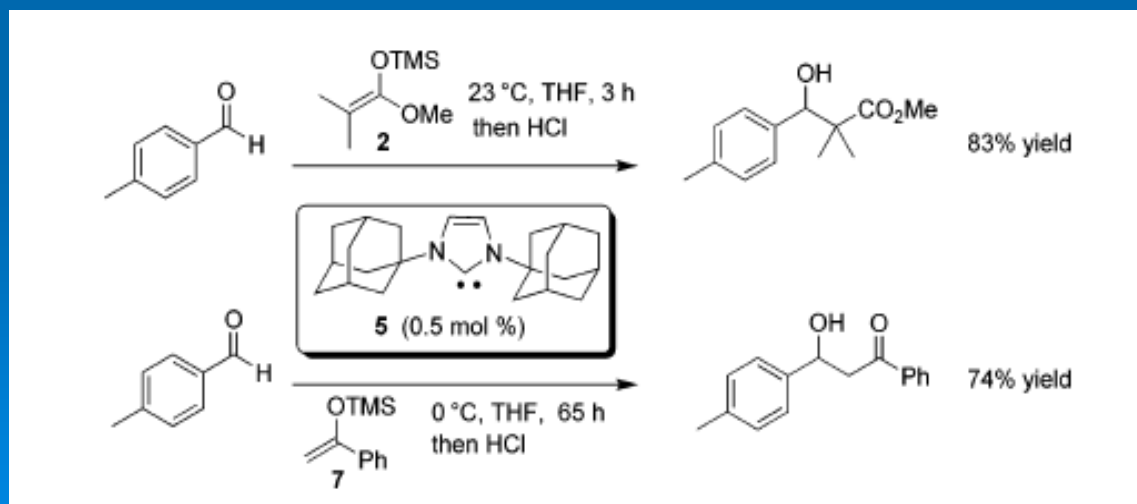
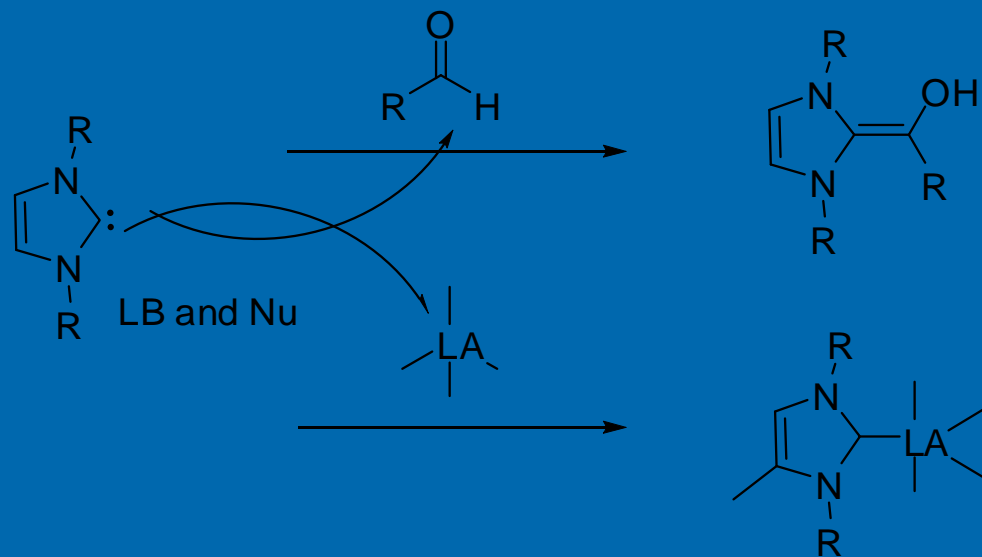


14) Bode, J. W. *et al.*, *J. Am. Chem. Soc.* **2007**, *129*, 3520-3521

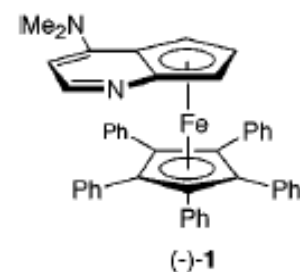
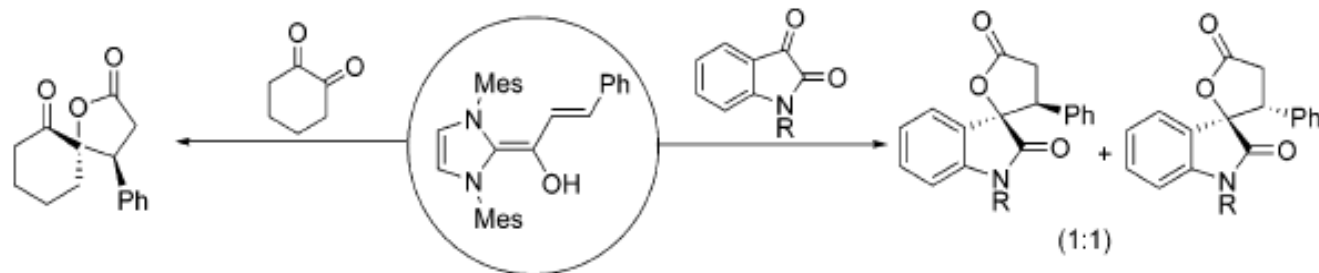
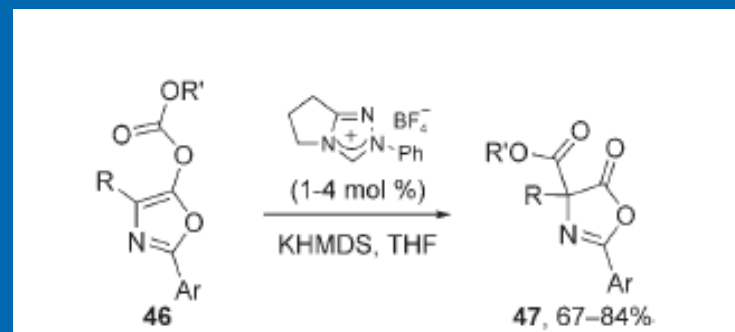
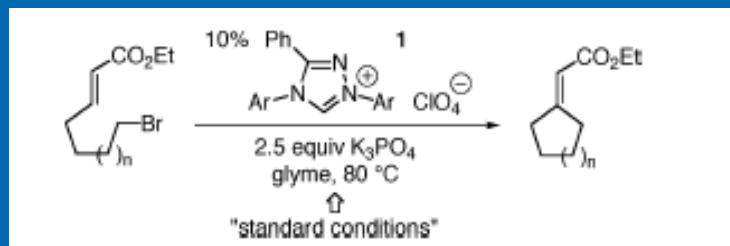
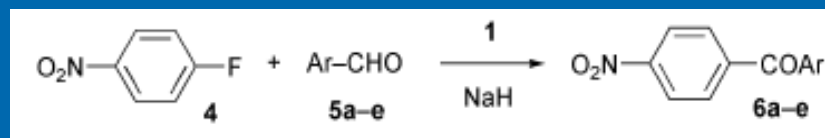
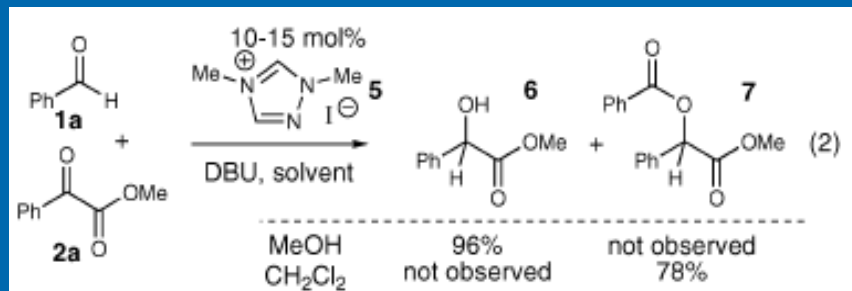




5. 逆回到原始，更有出路!



其它的一些反应



Fu, G. C

谢谢!

