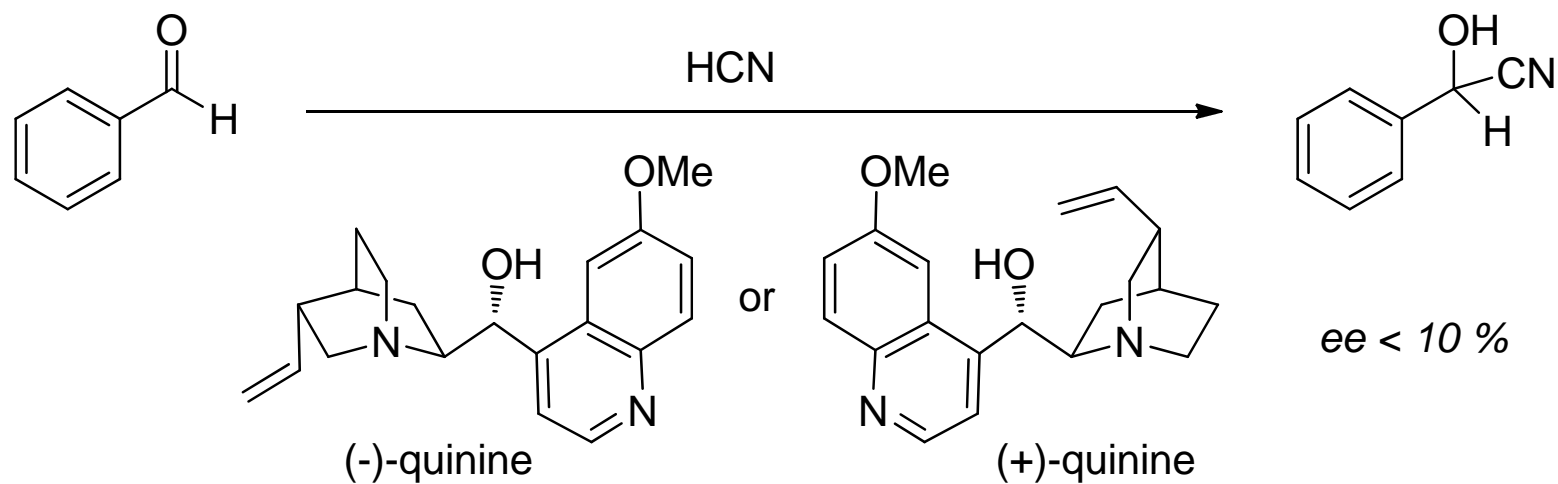


Chiral Amines as Catalysts in Asymmetric Synthesis

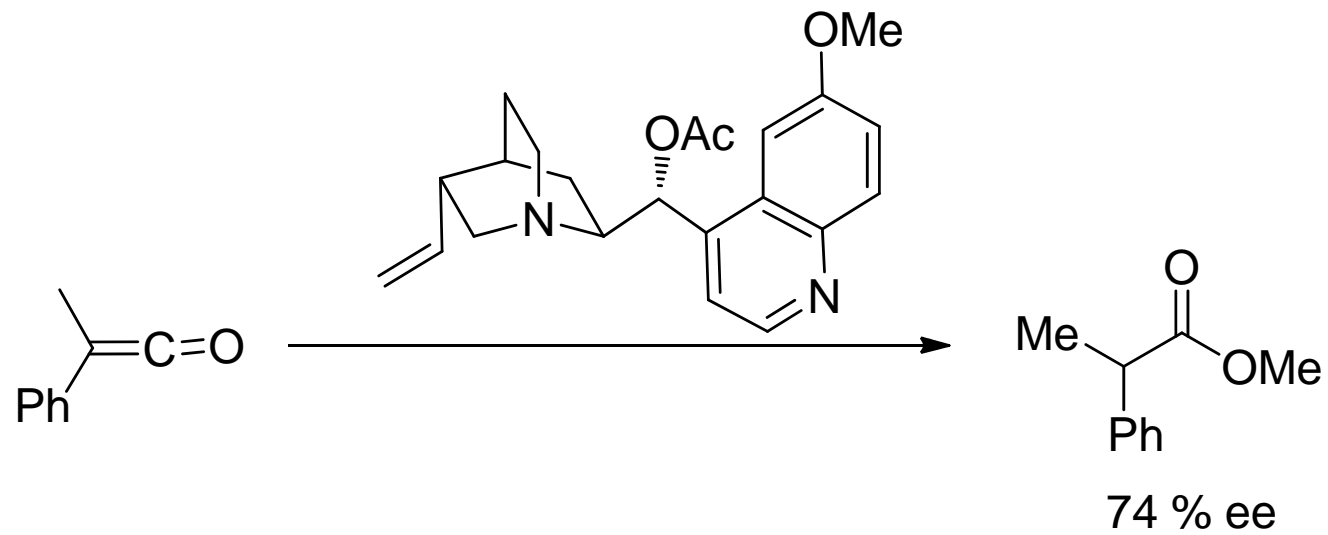
Rui, Zhang

2010-11-13

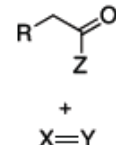
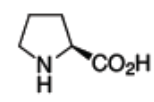
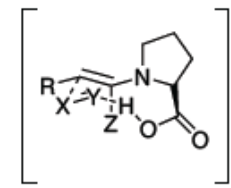
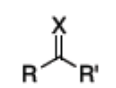
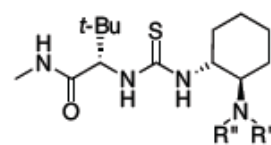
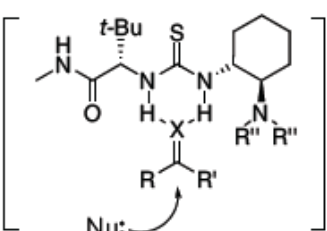
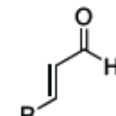
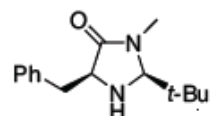
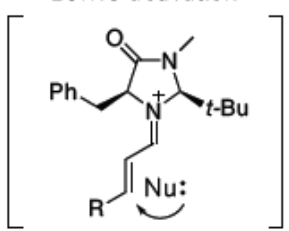
The First Chiral Amine Catalysts



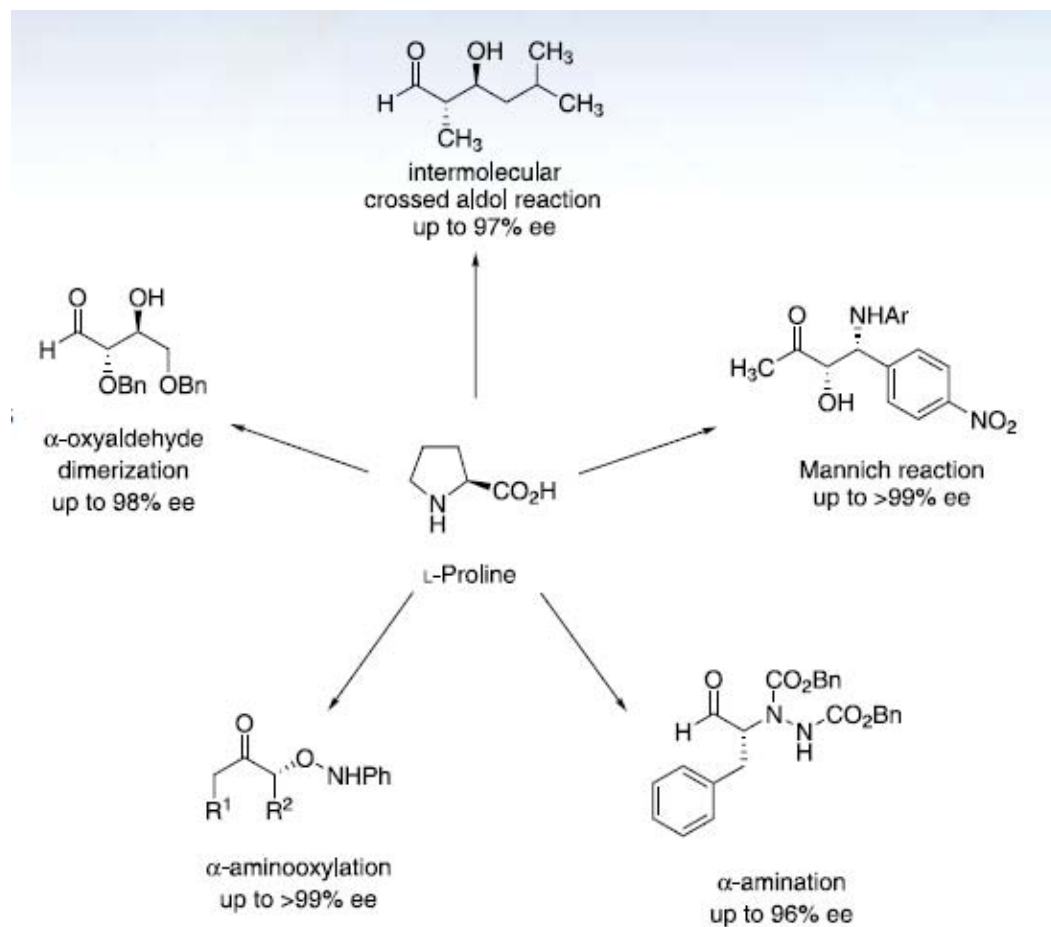
Breiding, G.,; Fiske, P. S. *Biochem. Z.* **1912**, 46, 7 .



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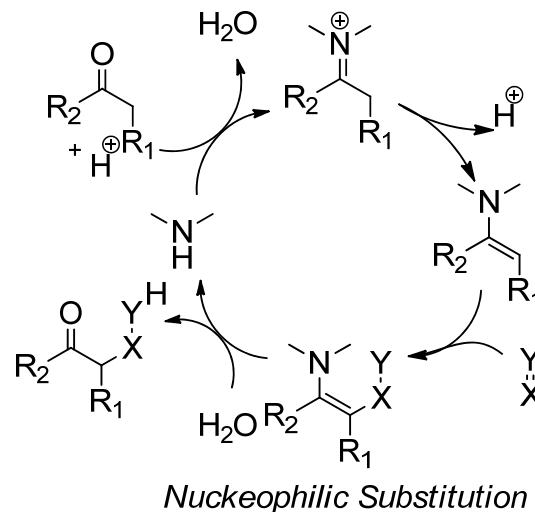
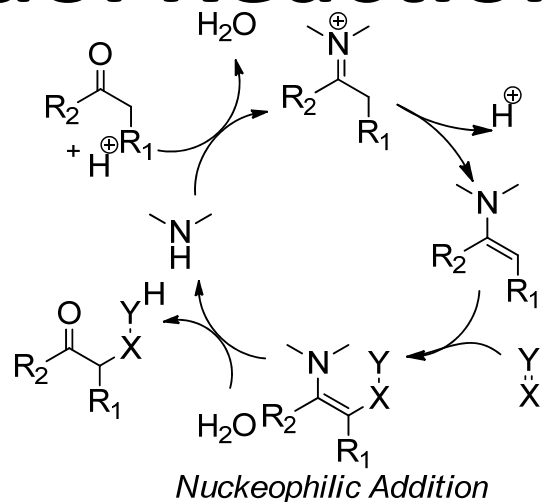
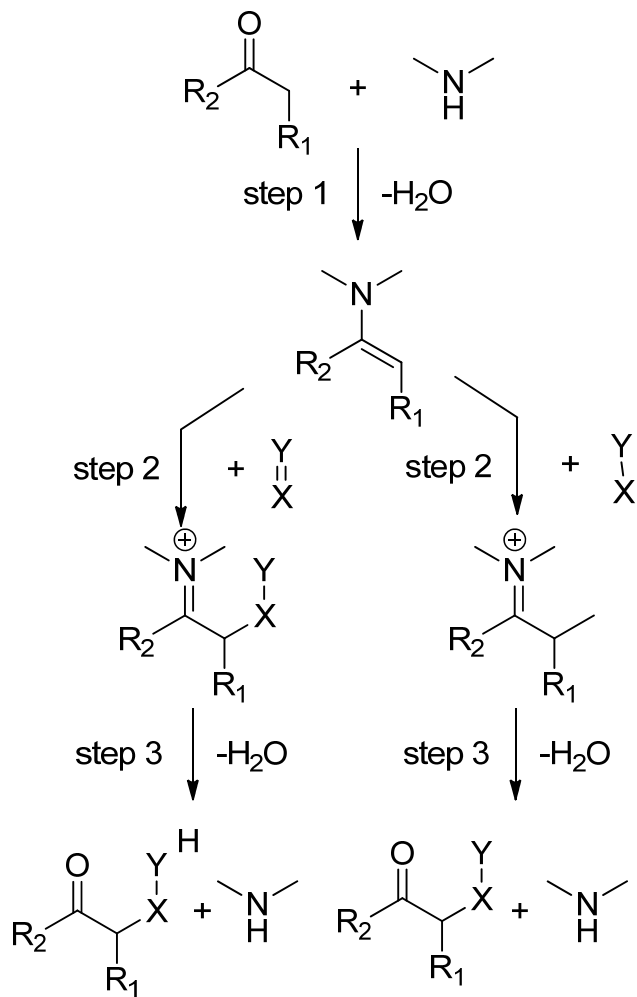
Substrate	Catalyst	Activation mode	Number of new reactions	Examples of new reaction variants
Enamine catalysis				
 <p>R = any organic chain or ring system X = C, N, O, S Y = generic organic atom Z = alkyl, H</p>		HOMO activation 	25	<ul style="list-style-type: none"> Aldehyde-aldehyde cross aldol coupling Intramolecular α-alkylation Mannich reaction Michael reaction α-Amination α-Oxygenation α-Halogenation α-Sulphenylation
Hydrogen-bonding catalysis				
 <p>X = O, NR R, R', R'' = alkyl, aryl</p>		LUMO activation 	30	<ul style="list-style-type: none"> Strecker reaction Mannich reaction Ketone cyanosilylation Biginelli reaction Pictet-Spengler reaction Reductive amination
Iminium catalysis				
 <p>R = alkyl, aryl</p>		LUMO activation 	50	<ul style="list-style-type: none"> Conjugate Friedel-Crafts reaction Ketone Diels-Alder reaction <i>exo</i>-Selective Diels-Alder reaction Mukaiyama-Michael reaction Conjugate hydride reduction Conjugate amination Conjugate oxygenation Conjugate sulphenylation Cyclopropanation Epoxidation, aziridination

MacMillan, D. W. C. *Nature* **2008**, 455.

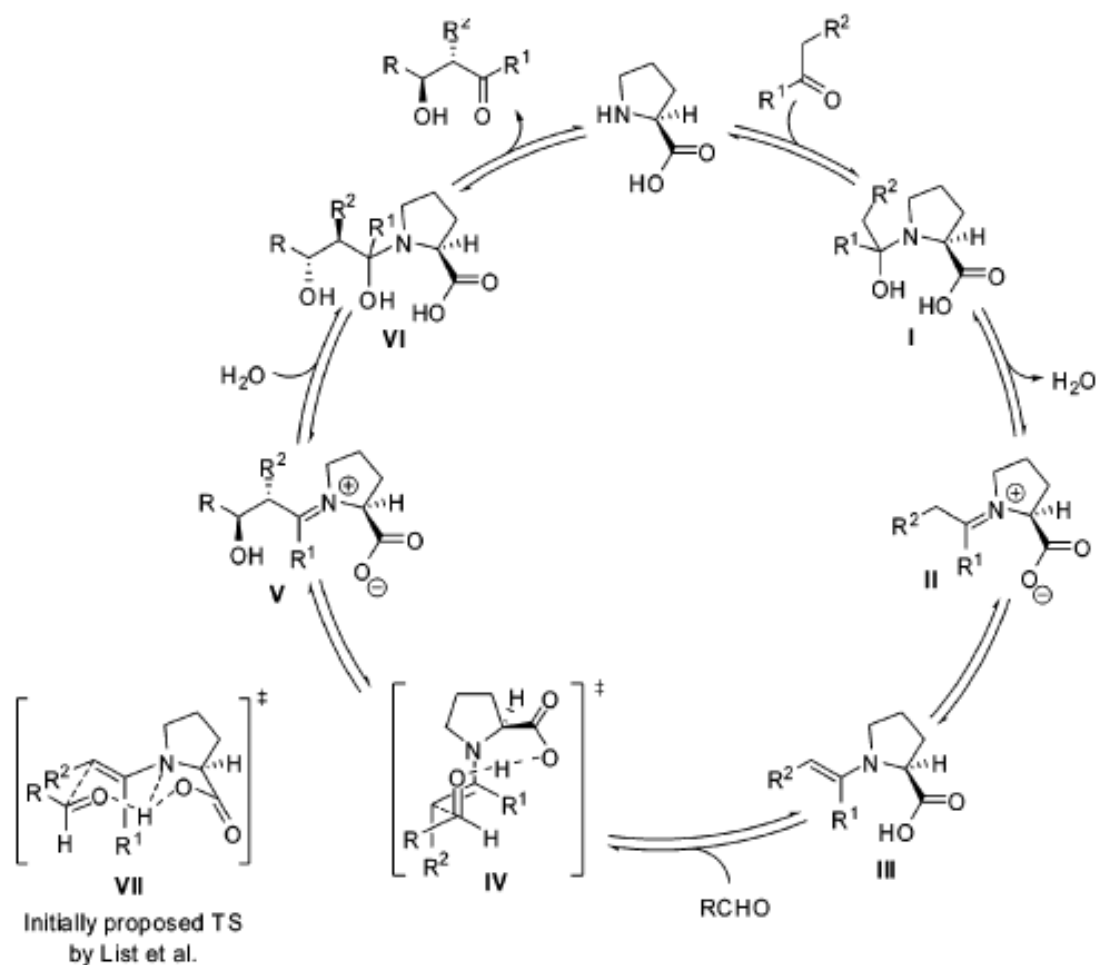


- (1) Northrup, A. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* 2002, 124, 6798.
 (2) List, B. et al. *J. Am. Chem. Soc.* 2002, 124, 827. (3) List, B. et al. *Org. Lett.* 2001, 3, 2423. (4) List, B. *J. Am. Chem. Soc.* 2002, 124, 5656. (5) Northrup, A. B. et al. *Angew. Chem., Int. Ed.* 2004, 43, 2152.

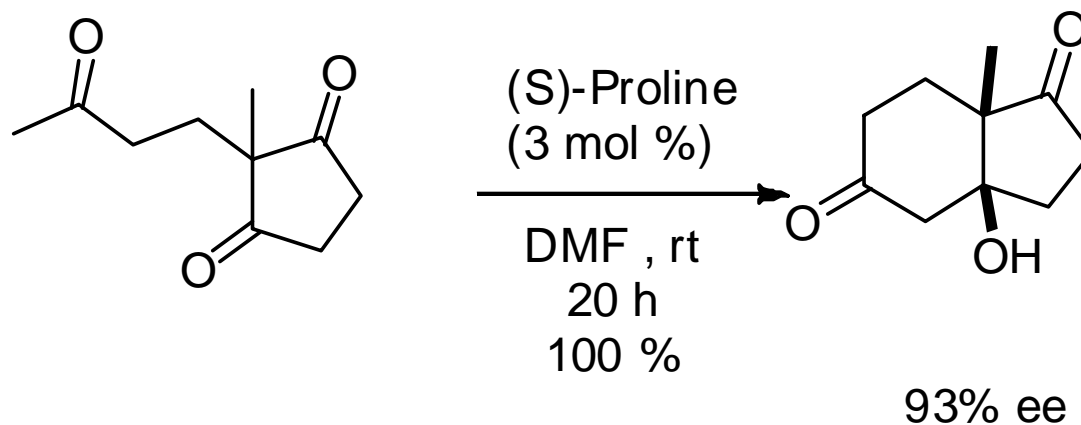
Asymmetric Aldol Reactions



Asymmetric Aldol Reactions

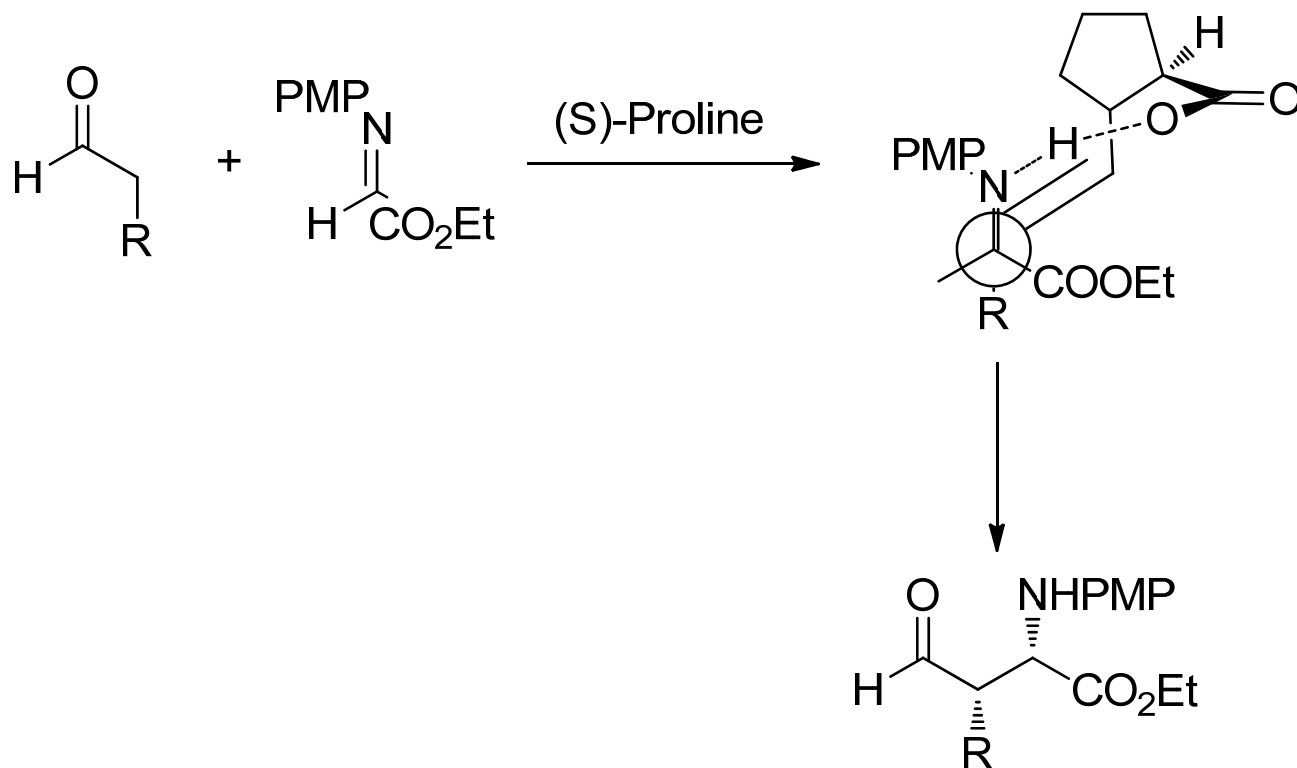


Asymmetric Aldol Reactions

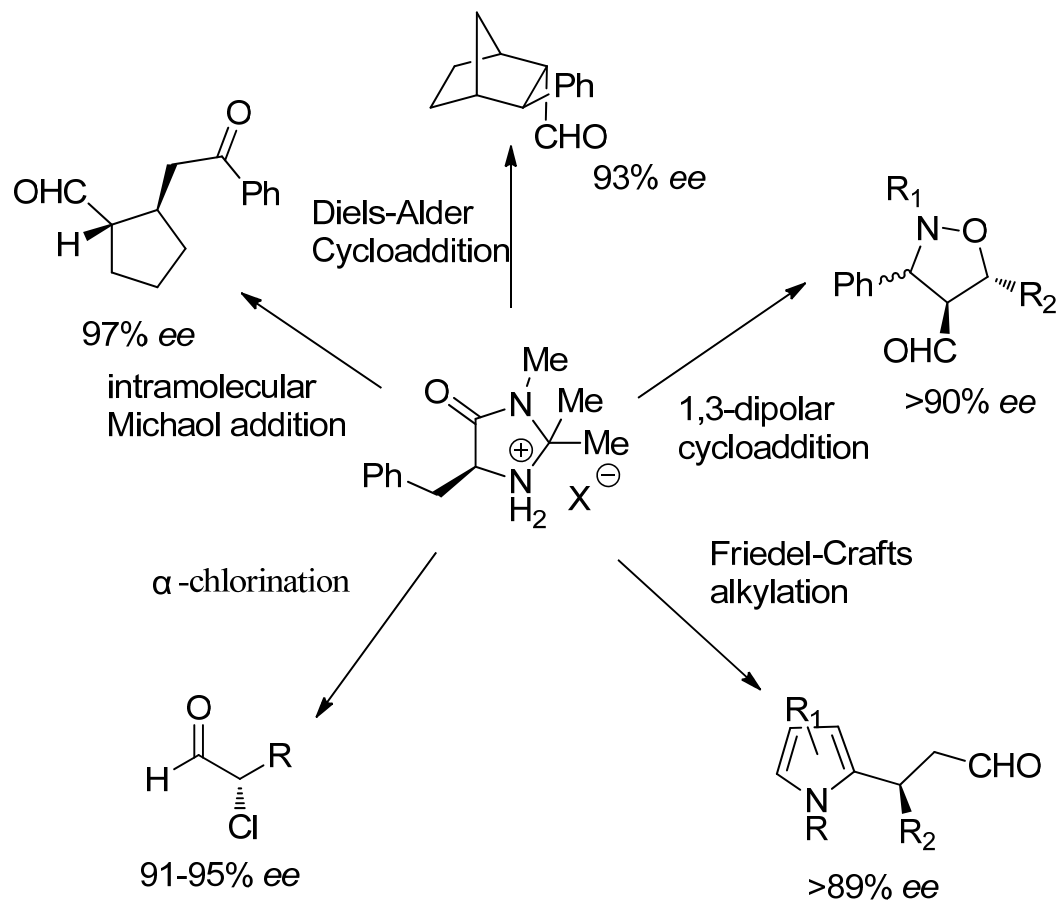


Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1974**, 39 1615

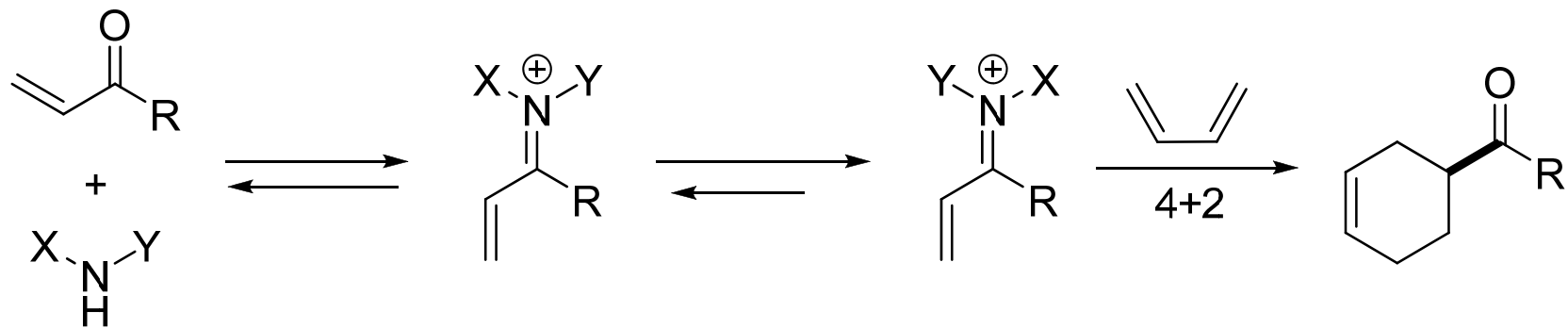
anti-Selective Mannich Reaction



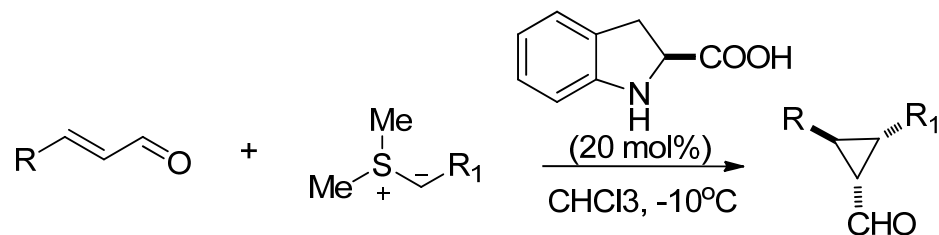
Imidazolidinon Organocatalysts



Cycloaddition

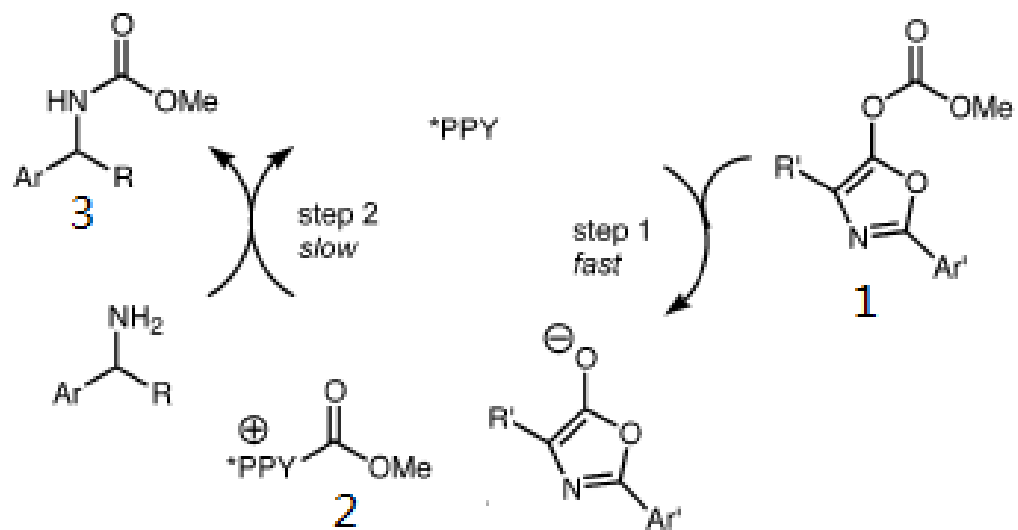
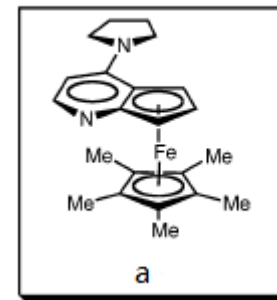
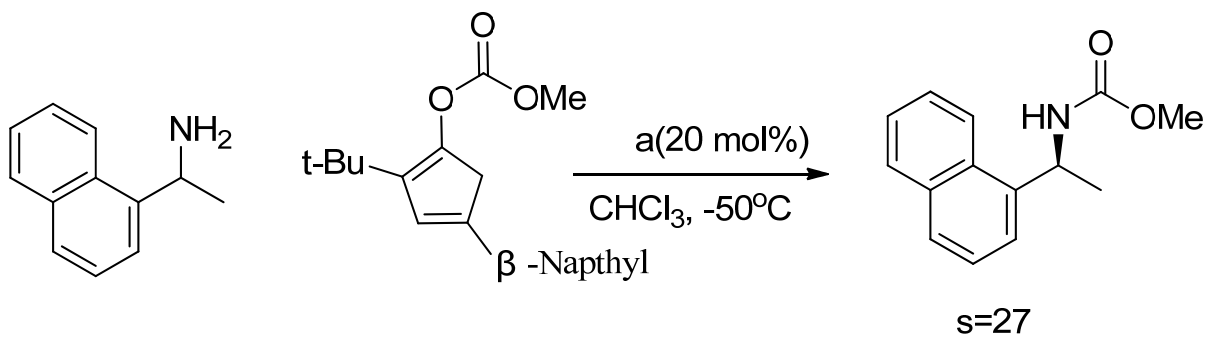


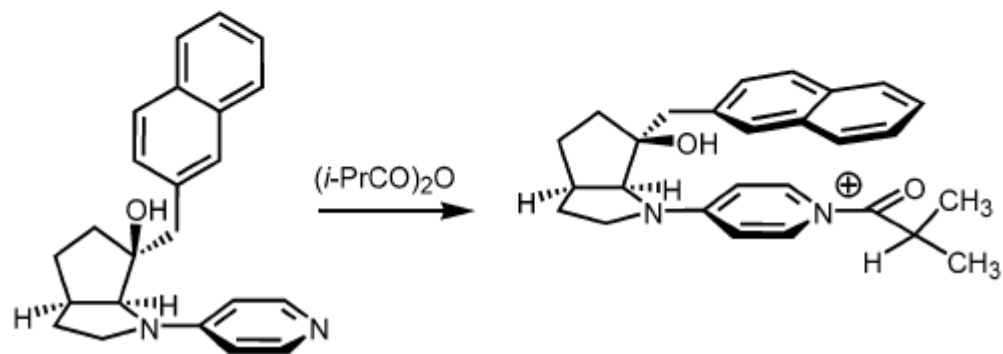
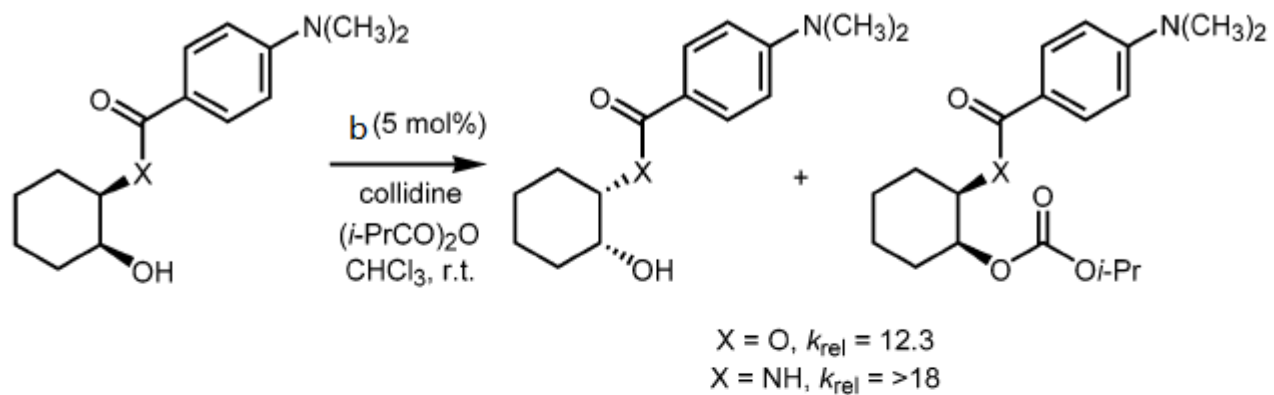
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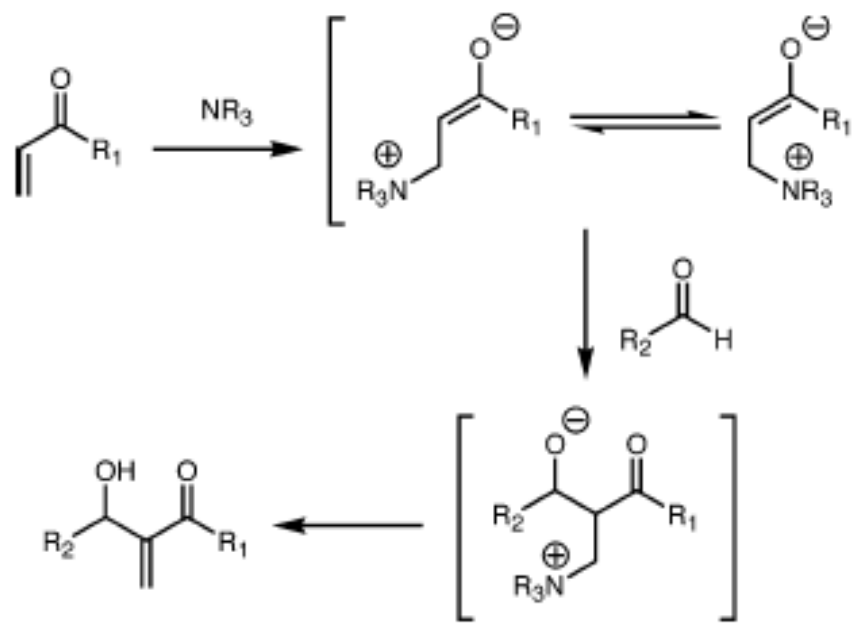


R	R ¹	Yield (%)	dr	ee ^b (%)
Pr	PhCO	85	30:1	95
allylOCH ₂	PhCO	77	21:1	91
Me	PhCO	67	>19:1	90 ^c
5-hexen-1-yl	PhCO	74	24:1	96
Ph	PhCO	73	33:1	89
<i>i</i> -Bu	PhCO	63	43:1	96
Pr	4-BrC ₆ H ₄ CO	67	72:1	92
Pr	4-MeOC ₆ H ₄ CO	64	>11:1	93
Pr	<i>t</i> -BuCO	82	6:1	95

Kunz, R. K.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2003**, 127, 3240.







- Thank you for your attention!