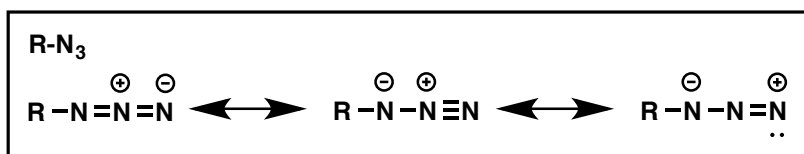


Reviews:

Brase et al. Organic Azides: An Exploding Diversity of a Unique Class of Compounds *ACIEE* **2005**, *44*, 5188

Gevorgyan et al. Transition-Metal-Catalyzed Denitrogenative Transannulation: Converting Triazoles into Other Heterocyclic Systems *ACIEE* **2012**, *51*, 862



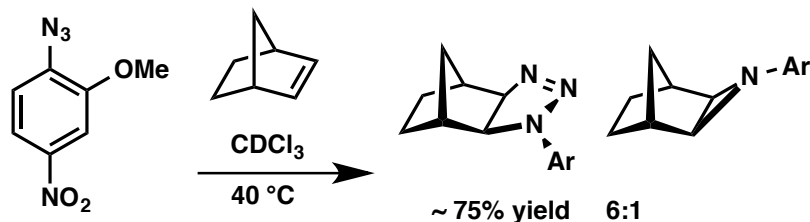
Huisgen reaction
Huisgen *ACIEE* **1963**, *2*, 565

dipoles: $R-N_3$

dipolarophiles: alkene or alkyne

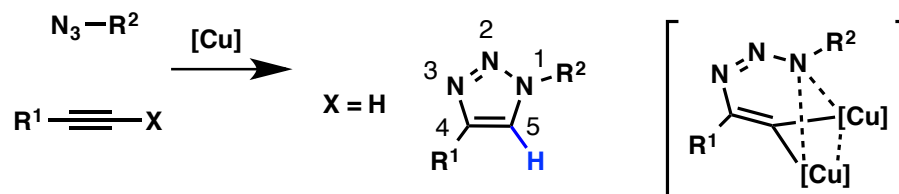
1. terminal alkenes react extremely slowly
2. electron-deficient and electron-rich alkenes/alkynes
3. strained olefins or alkynes

Schmidt rearrangement
Curtius rearrangement
Staudinger reaction

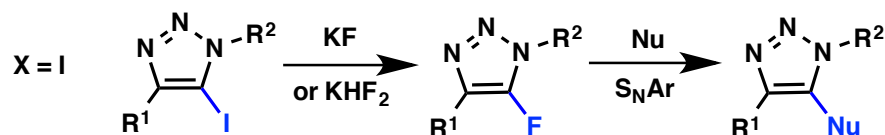


Brase et al. *Chem. Commun.* **2002**, 1296

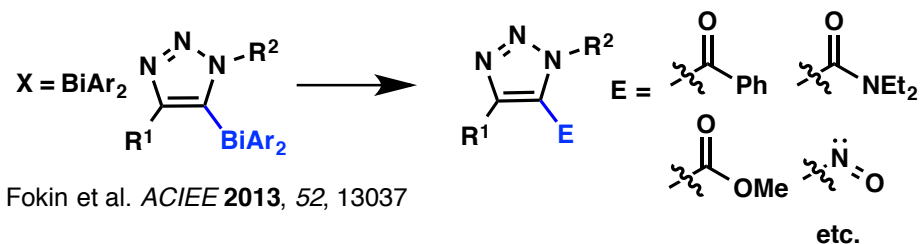
[Cu] = CuI, CuSO₄, CuOTf etc.



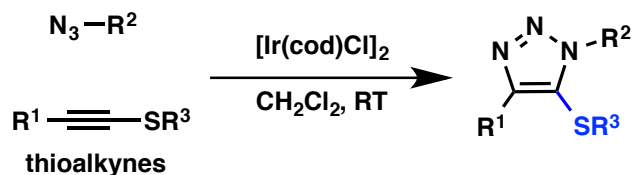
Fokin, Sharpless et al. *ACIEE* **2002**, *41*, 2596
Fokin et al. *Science* **2013**, *340*, 457



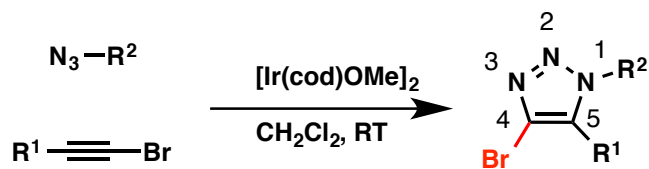
Fokin et al. *ACIEE* **2012**, *51*, 11791



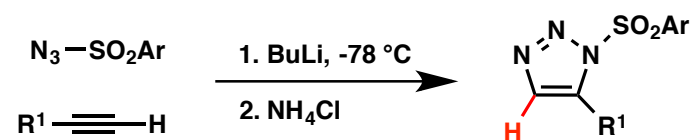
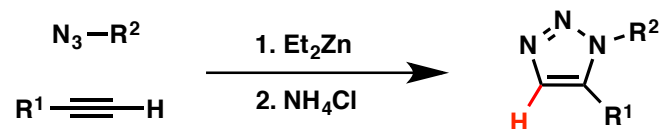
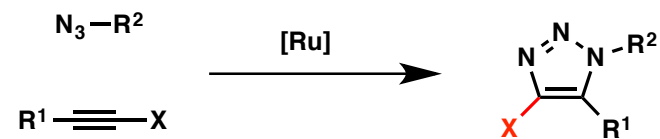
Fokin et al. *ACIEE* **2013**, *52*, 13037



thioalkynes

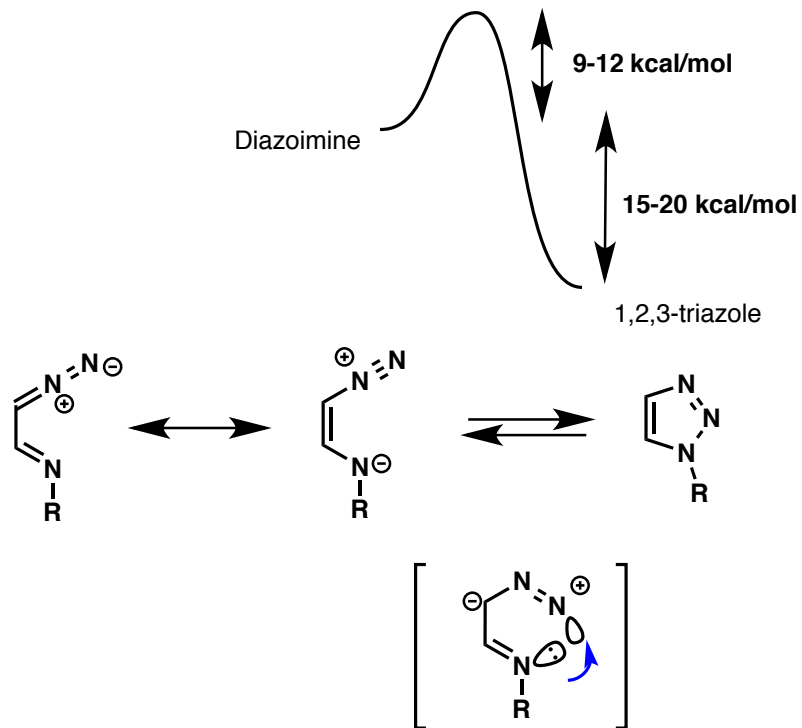
 $\text{R}^1, \text{R}^2, \text{R}^3 = \text{alkyl, aryl}$ 

bromoalkynes

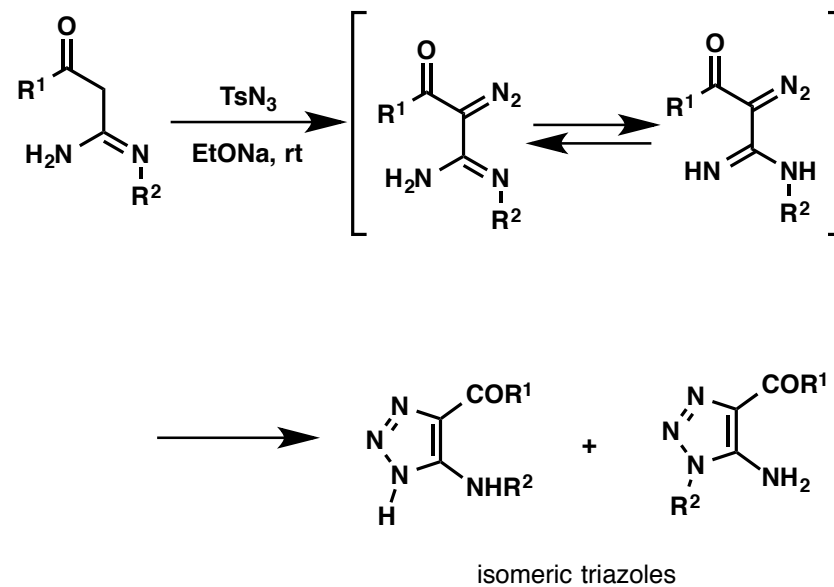
 $\text{R}^1, \text{R}^2, \text{R}^3 = \text{alkyl, aryl}$ Taran et al. *OL* **2013**, *15*, 4698Jia, Sun, and Lin et al. *JOC* **2014**, *79*, 11970Caoatt et al. *OL* **2011**, *13*, 2984Greaney et al. *OL* **2013**, *15*, 4826 $\text{X} = \text{H, alkyl, aryl}$ $[\text{Ru}] = \text{Cp}^*\text{RuCl}(\text{PPh}_3)_2, \text{Cp}^*\text{RuCl}(\text{cod}), [\text{Cp}^*\text{RuCl}]_4$ Lin, Jia, Fokin et al. *JACS* **2008**, *130*, 8923Taddei et al. *JOC* **2015**, *80*, 2562

Ring Chain Tautomerism (Diazoimine – 1,2,3-Triazole Equilibrium)

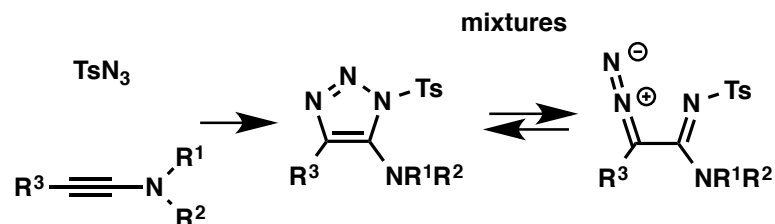
Diazoimine – 1,2,3-triazole equilibrium

The heteroelectrocyclic
(pseudopericyclic) mechanism

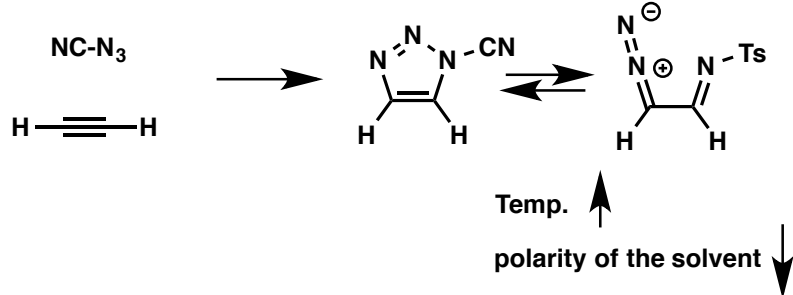
Reaction of acetamides with tosyl azide



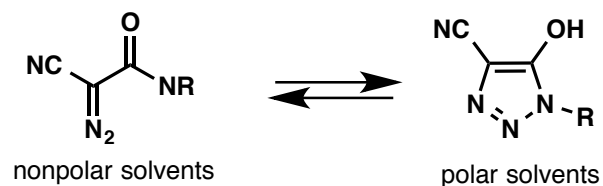
Reaction of ynamines with tosyl azide

Haron, Stanley, and Gupta et al. *JOC* 1970, 35, 3444

Cycloaddition of cyanogen to acetylene

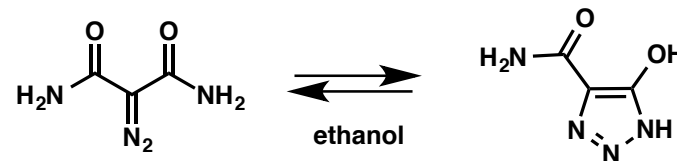


The constants of equilibrium between diazo compounds and triazoles

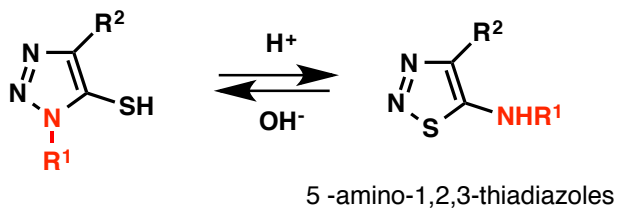
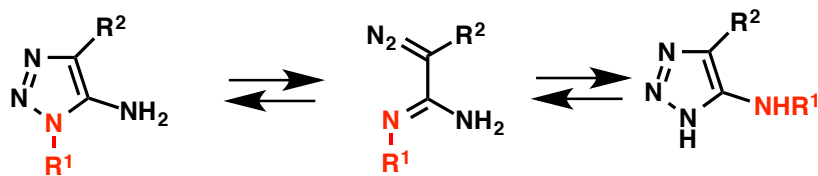
 $K = [\text{diazo compounds}]/[\text{triazoles}]$ at 35 °C in various solvents

R	D ₂ O	CD ₃ CN	DMSO-D ₆	Acetone-D ₆	C ₆ D ₆	C ₂ D ₅ OD
4-MeO-C ₆ H ₄	>100		21 ± 3	16 ± 1	0.7 ± 0.1	16 ± 2
Me	45.4 ± 2.1	27 ± 2	3.2 ± 0.8	1.2 ± 0.2	0.3 ± 0.02	11 ± 1
Bn	60 ± 9		6.2 ± 0.2	1.5 ± 0.2	0.24 ± 0.03	19.0 ± 0.8

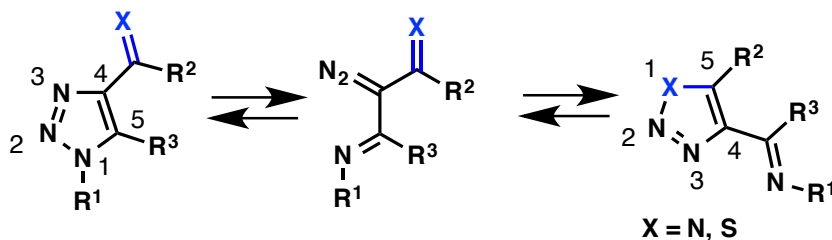
Tautomerism in the diazomaloamide – 5-hydroxy-1,2,3-triazole



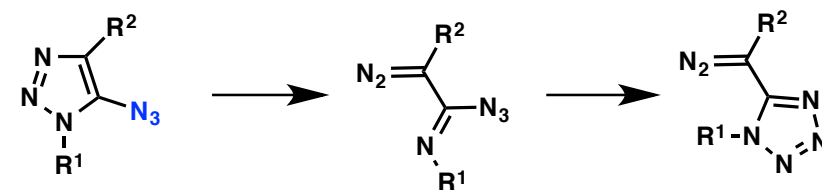
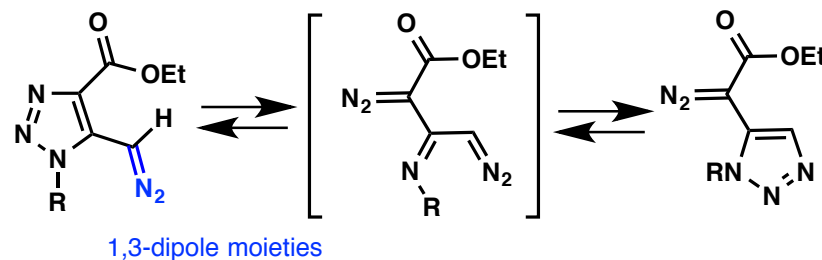
Dimroth Type Rearrangement



Cornforth-Type Rearrangements

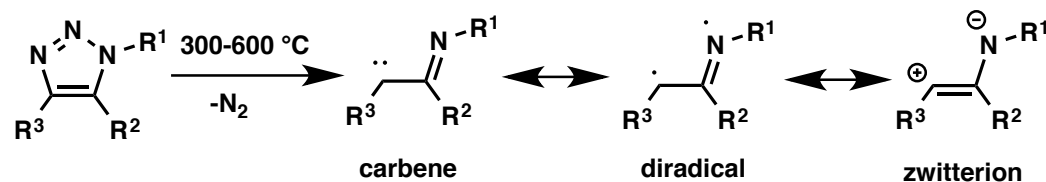


L'abbe' Type Rearrangements

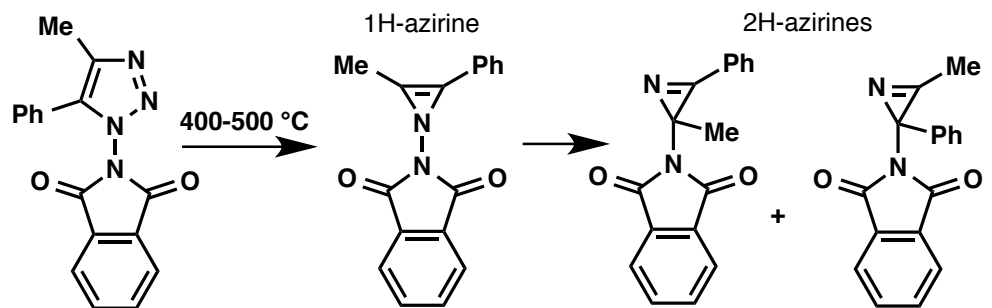


- L'abbe' et al. *J. Heterocycle Chem.* **1984**, *21*, 627
 L'abbe' et al. *Tetrahedron* **1988**, *44*, 461
 L'abbe' et al. *J. Heterocycle Chem.* **1989**, *26*, 701
 Dankova et al. *Tetrahedron* **1989**, *45*, 7329
 L'abbe' et al. *J. Heterocycle Chem.* **1990**, *27*, 2021
 L'abbe' et al. *Bull Soc Chim Belg.* **1990**, *99*, 281
 L'abbe' et al. *Bull Soc Chim Belg.* **1990**, *99*, 833
 Martvin et al. *Chem. Zvesty* **1979**, *10*, 514

Thermolysis of 1,2,3-Triazoles



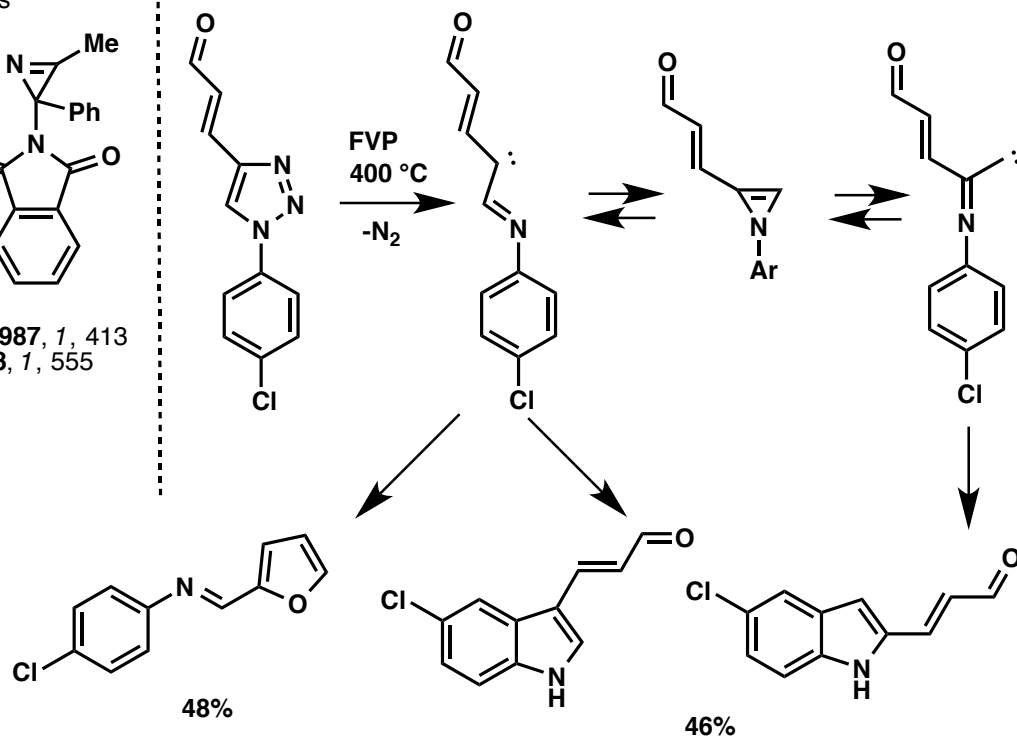
Vacuum pyrolysis of trisubstituted triazoles



1-N-phthalimido-1,2,3-triazole

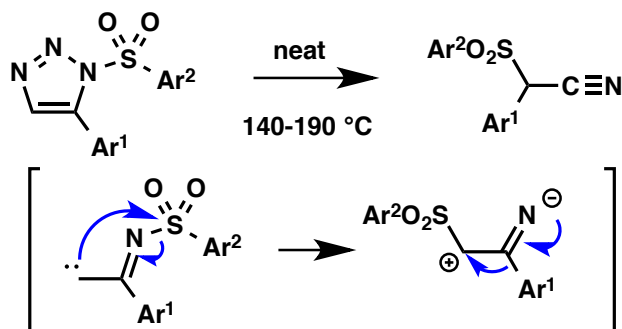
Rees et al. *J. Chem. Soc. Perkin. Trans.* **1987**, *1*, 413
 Rees et al. *Chem. Soc. Perkin Trans.* **1973**, *1*, 555

Flash vacuum pyrolysis of 4-acroleinyl-1-aryl-1,2,3-triazoles

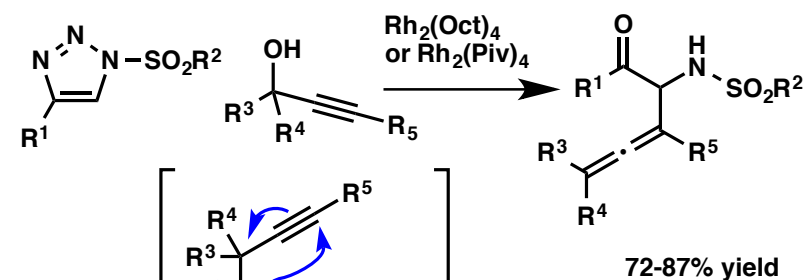
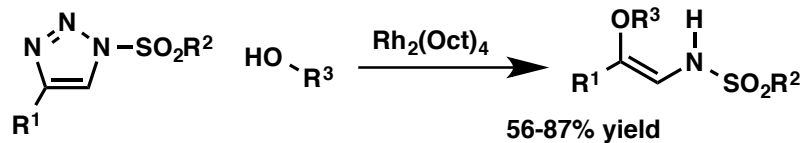
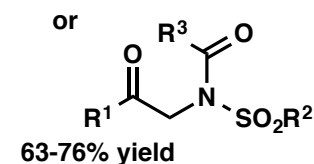
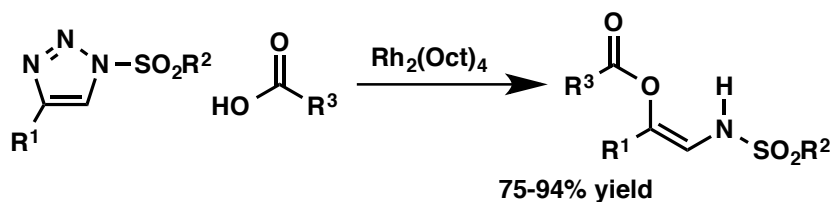
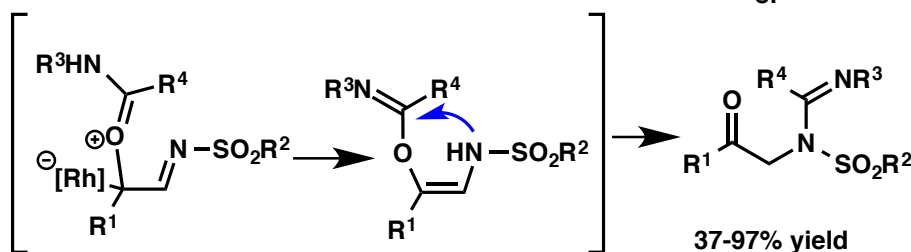
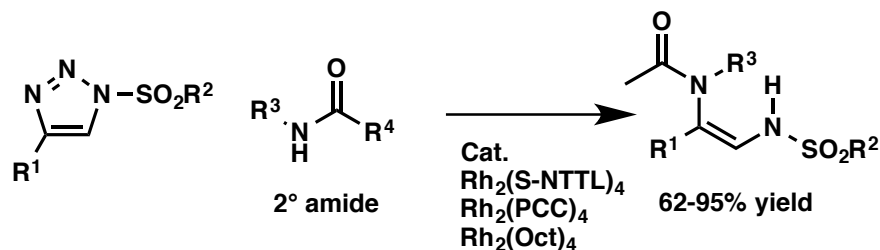
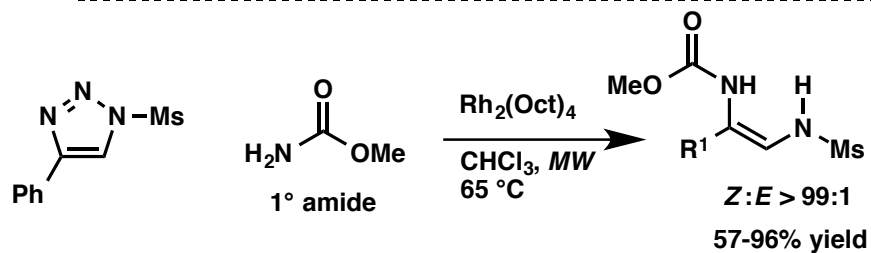
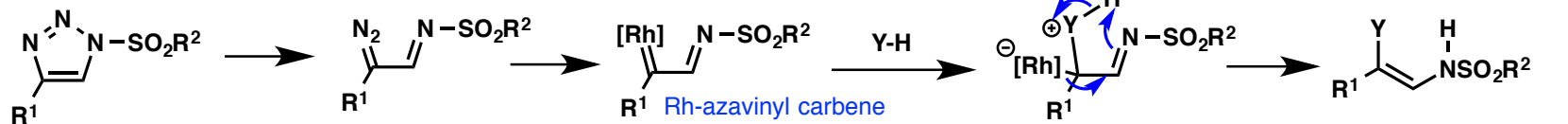
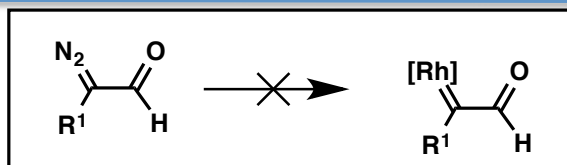


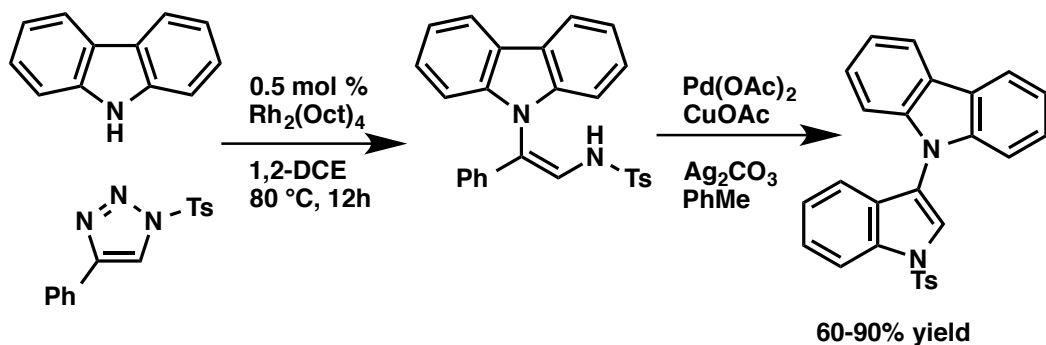
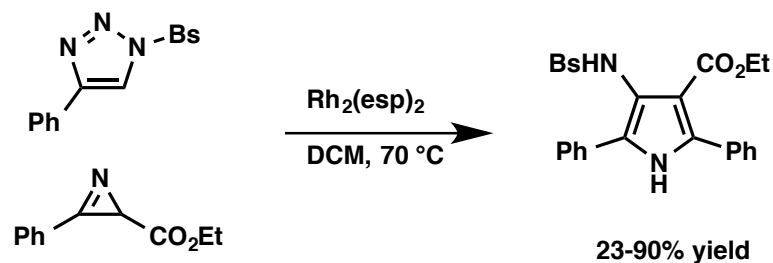
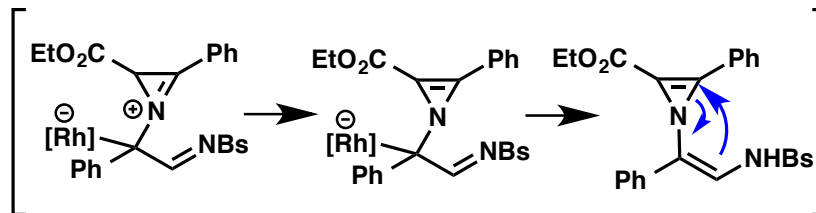
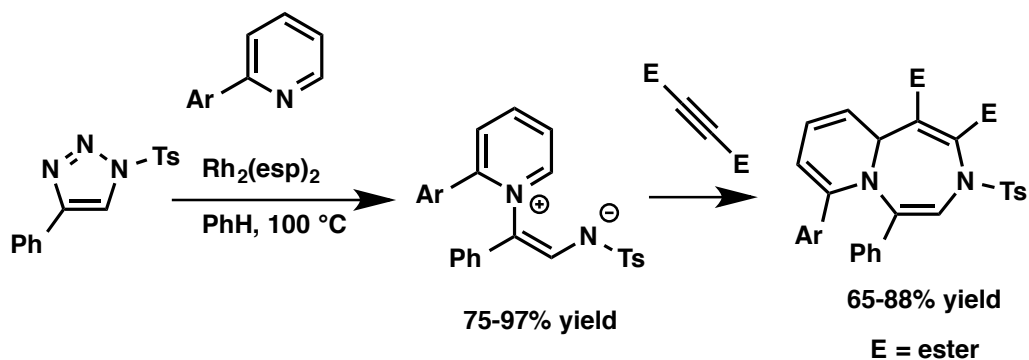
Riedl et al. *Tetrahedron* **2012**, *68*, 1299

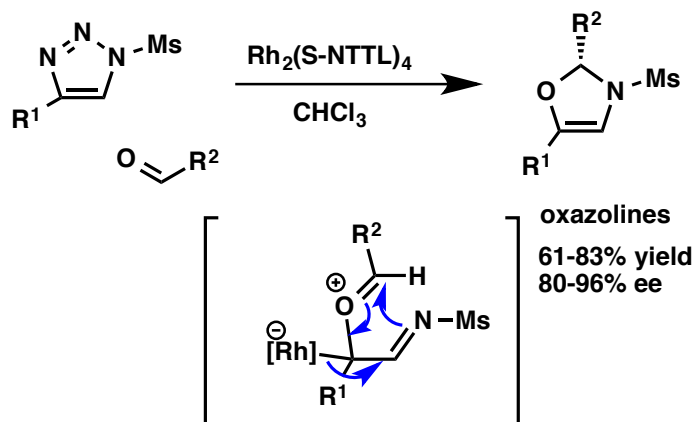
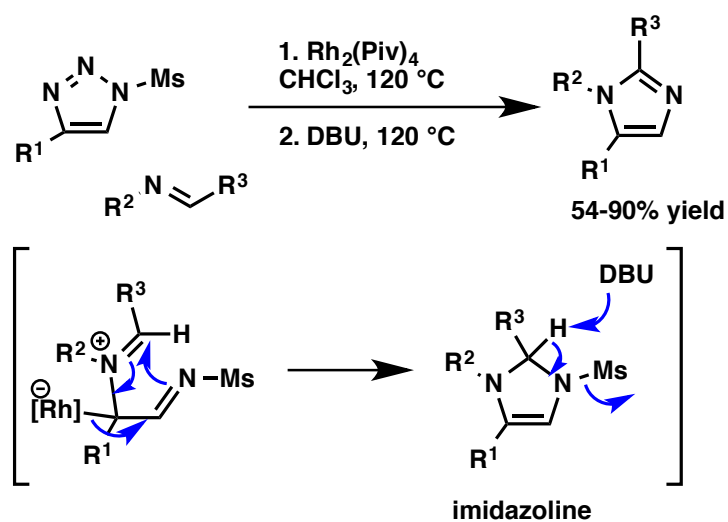
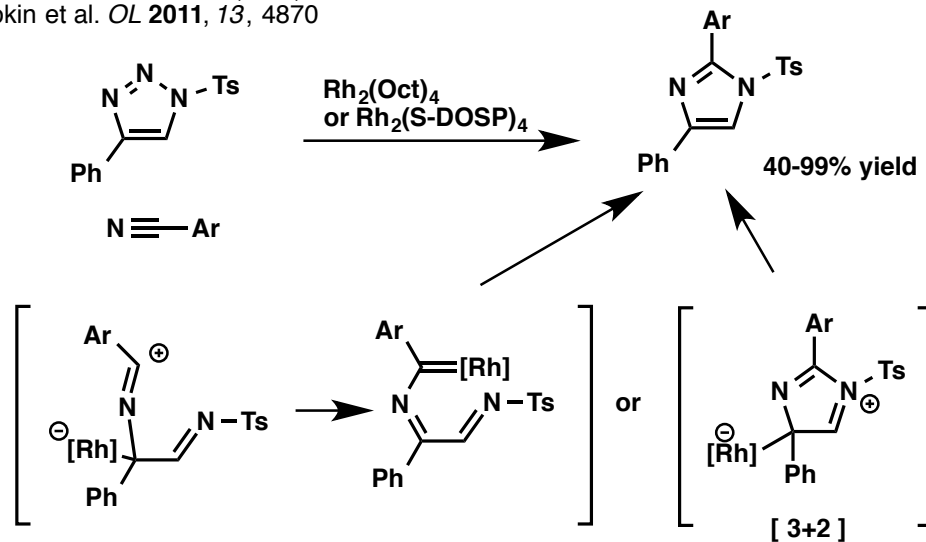
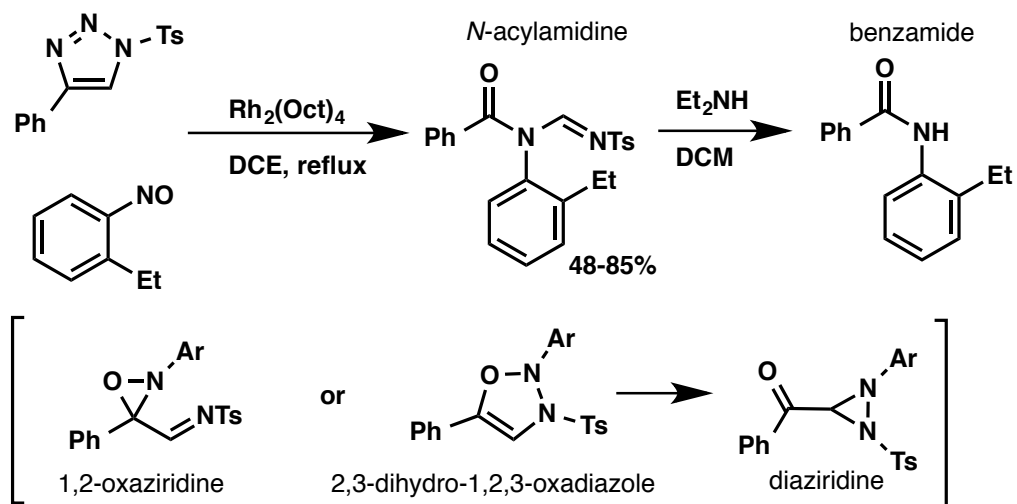
Formation of sulfonyl nitriles

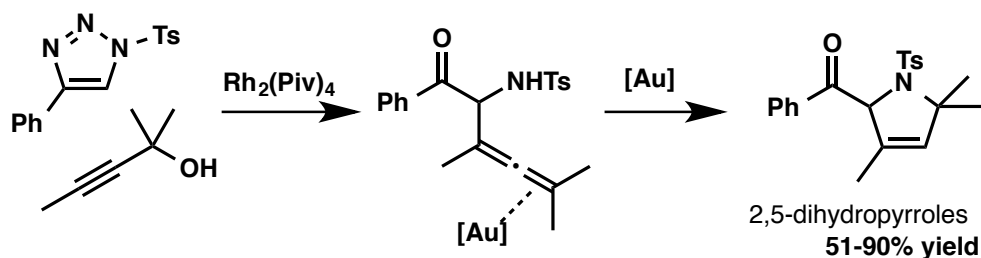
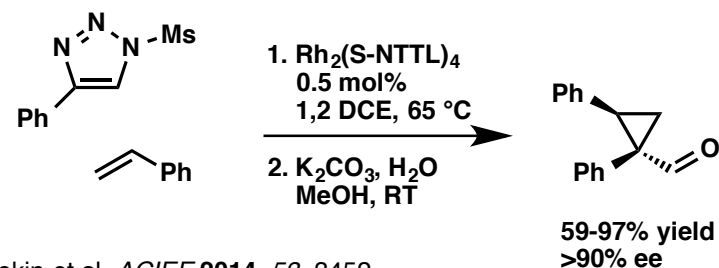
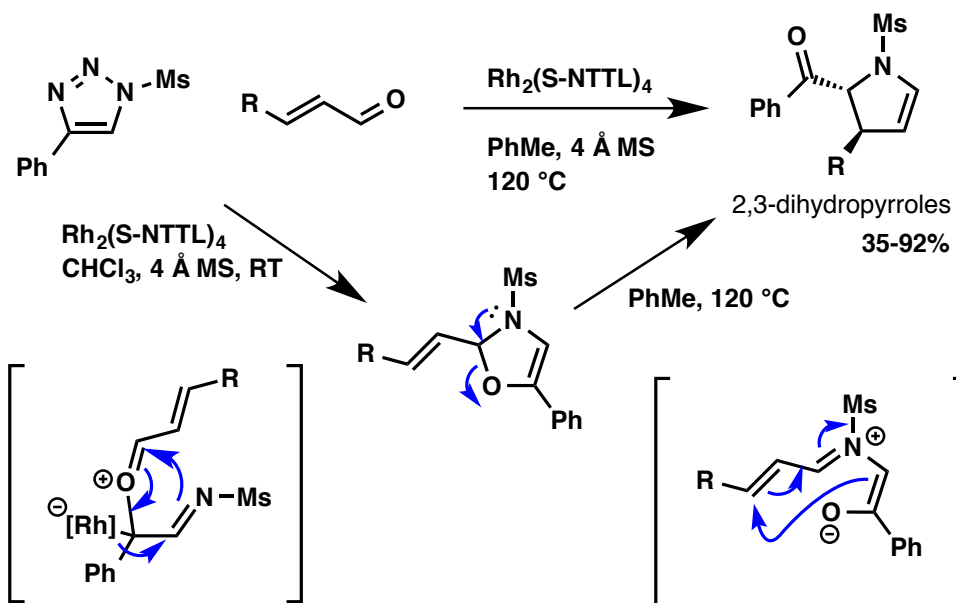
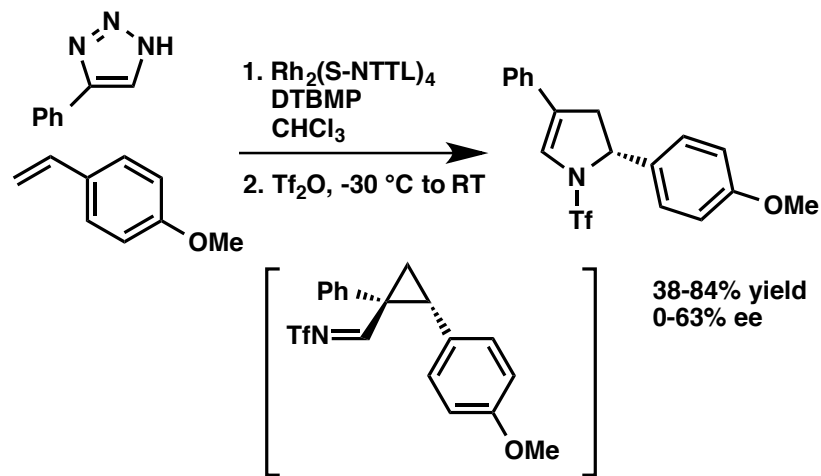


Croatt et al. *Tetrahedron* **2013**, *69*, 7840

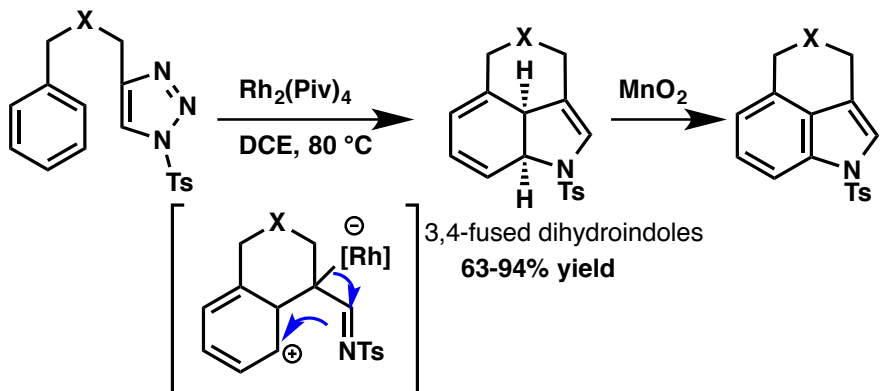
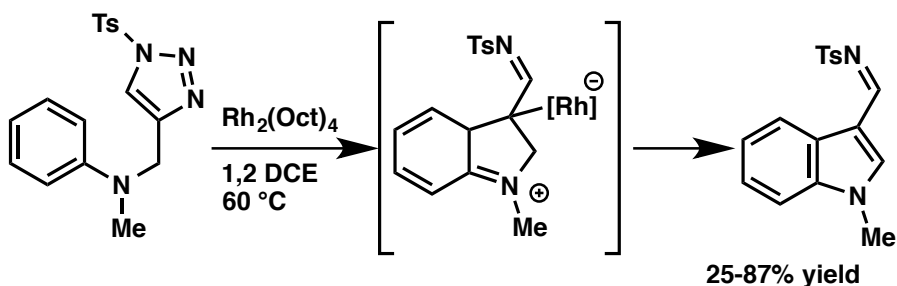
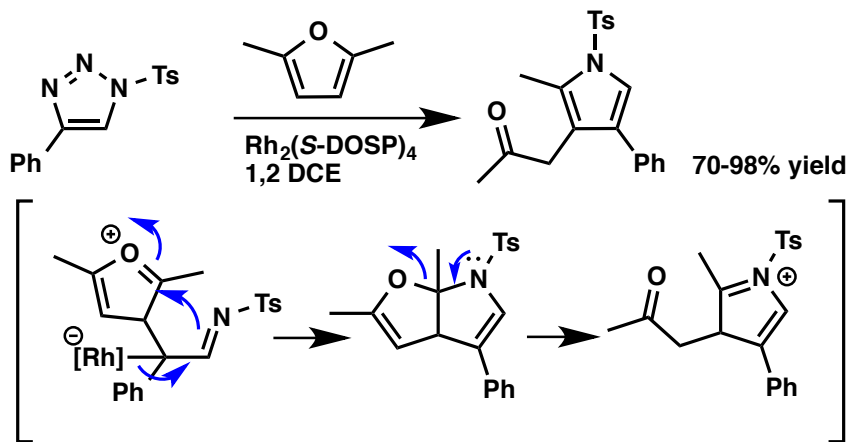
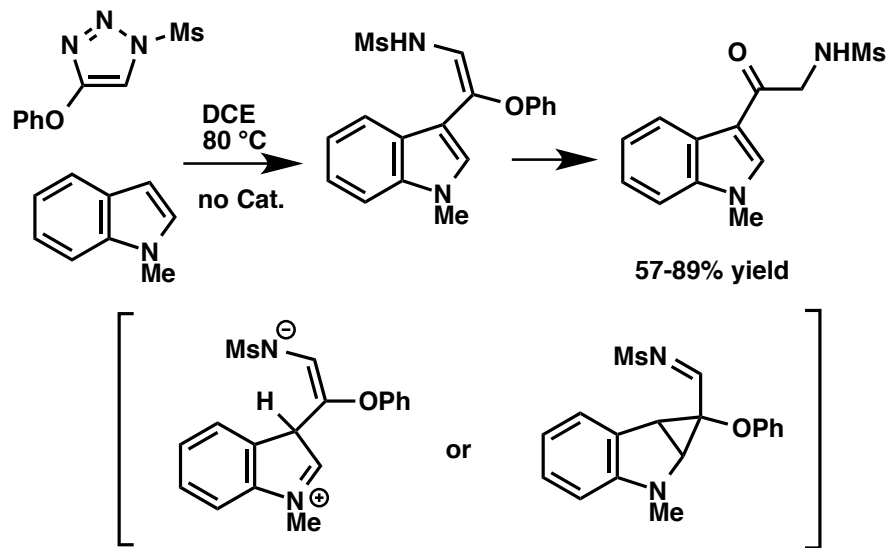
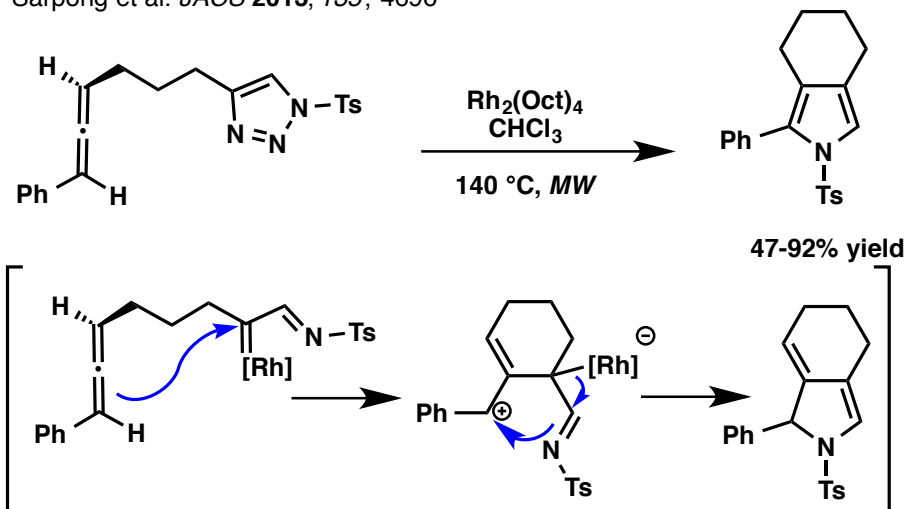
Fokin et al. *JACS* 2014, 136, 195

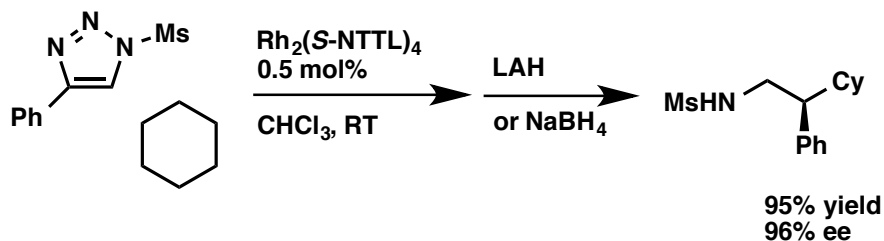
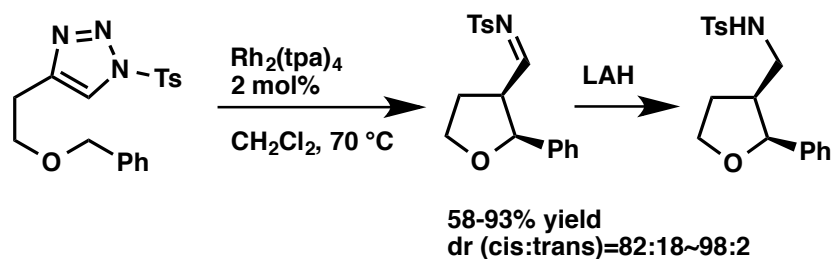
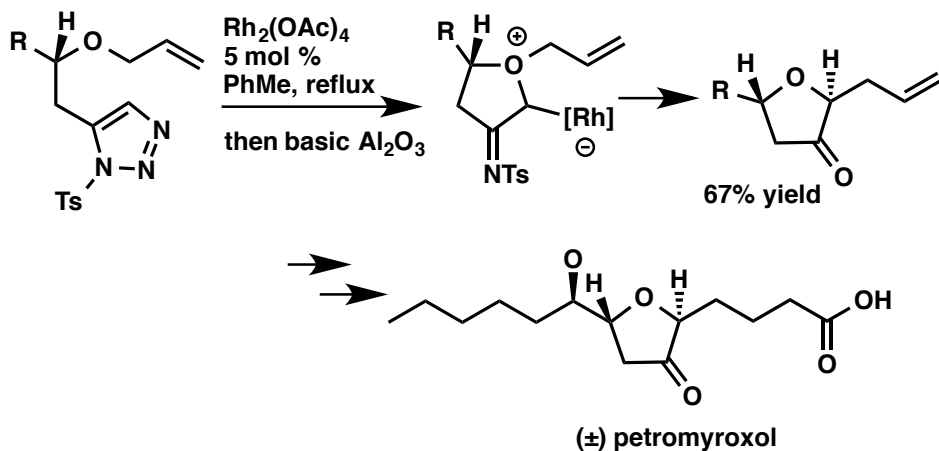
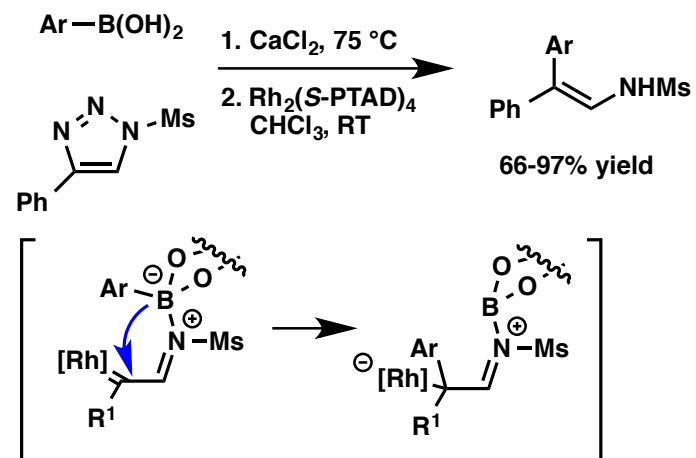
Yoo et al. *OL* 2015, 17, 1830Tang, Shi, et al. *Chem. Eur. J.* 2015, 21, 3562Yoo et al. *JACS* 2014, 136, 11606

Fokin et al. *ACIEE* 2013, 52, 150Fokin et al. *JACS* 2008, 130, 14972Fokin et al. *OL* 2011, 13, 4870Li et al. *OL* 2014, 16, 6394

Miura and Murakami. et al. *Chem. Eur. J.* **2014**, *20*, 16078Fokin et al. *JACS* **2009**, *131*, 18034
JACS **2010**, *132*, 2510
OL **2011**, *13*, 4870
OL **2011**, *13*, 4578
ACIEE **2014**, *53*, 3452Miura and Murakami et al. *JACS* **2013**, *135*, 13652Fokin et al. *ACIEE* **2014**, *53*, 3452

DTBMP: 2,6-di-tert-butyl-4-methyl pyridine

Miura and Murakami et al. *JACS* 2014, 136, 2272Lin et al. *OL* 2014, 16, 3752Davis et al. *JACS* 2013, 135, 4716Davis et al. *JACS* 2014, 136, 10266Sarpong et al. *JACS* 2013, 135, 4696

Fokin et al. *JACS* 2011, 133, 10352Sarpong et al. *JACS* 2015 DOI:10.1021/jacs.5b04295Boyer *JOC* 2015, 80, 4771Fokin et al. *JACS* 2012, 134, 14670Fokin et al. *ACIEE* 2012, 51, 13054Miura and Murakami et al. *JACS* 2012, 134, 17440