

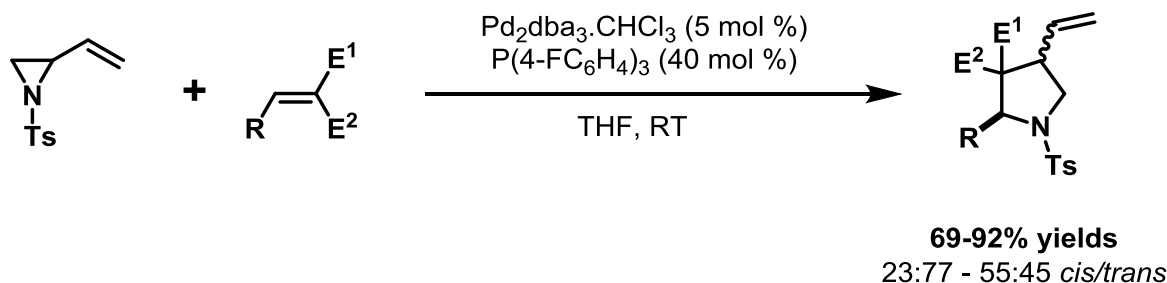
# The Divergent Synthesis of Nitrogen Heterocycles by Rhodium(I)- Catalyzed Intermolecular Cycloadditions of Vinyl Aziridines and Alkynes

J. J. Feng, T.-Y. Lin, C.-Z. Zhu, H. Wang, H.-H. Wu and J. Zhang\*  
*J. Am. Chem. Soc.* **2016**, asap

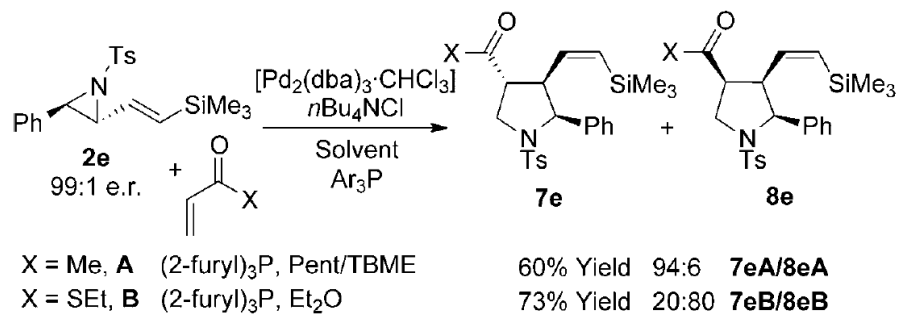
DOI: 10,1021/jacs.6b00386

# State of the art

- (3+2) cycloaddition



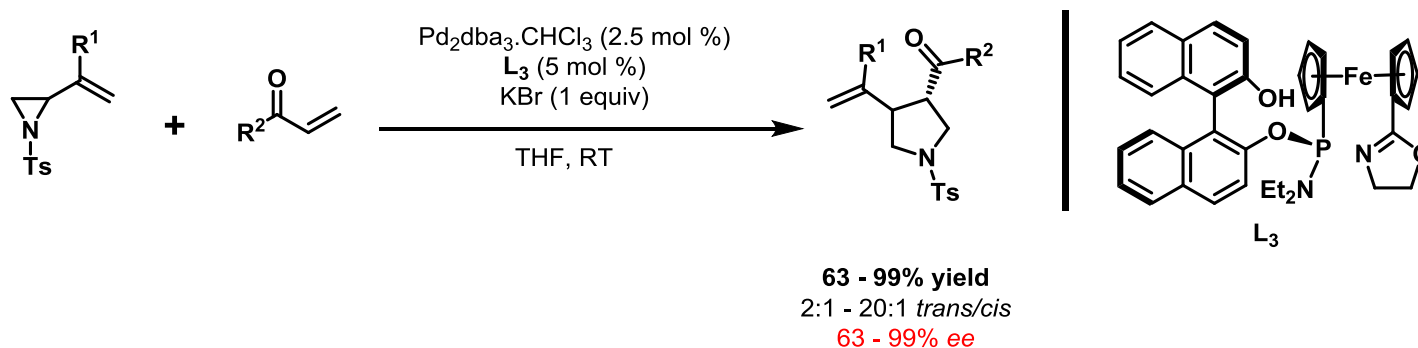
Yamamoto, *J. Org. Chem.* **2002**, 5977



Aggarwal, *Angew. Chem. Int. Ed.* **2011**, 6370

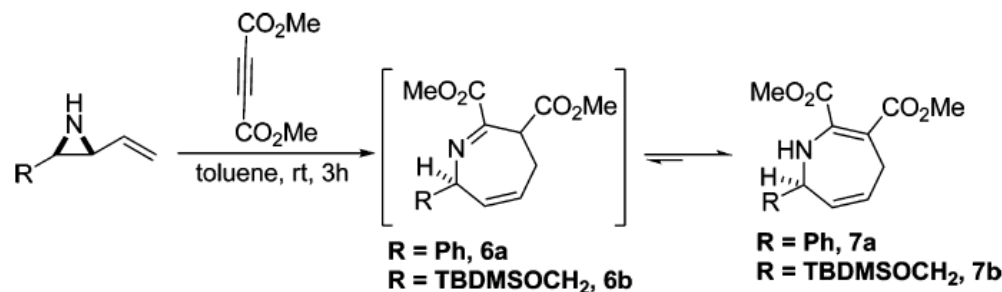
# State of the art

- (3+2) cycloaddition



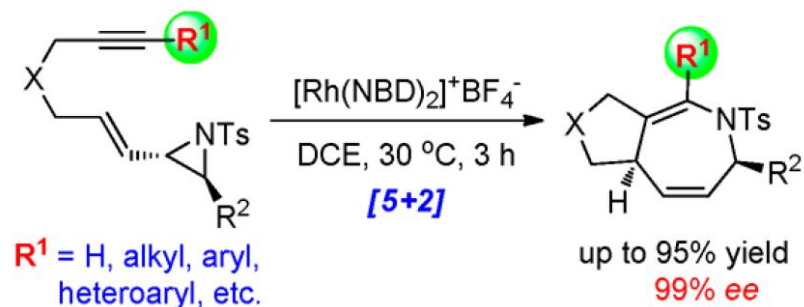
Hou & Ding, *Angew. Chem. Int. Ed.* **2011**, 6370

- (5+2) cycloaddition

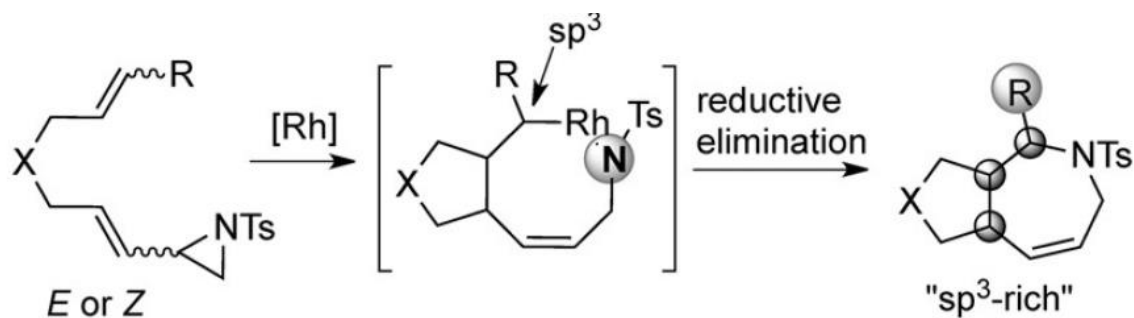


Yudin, *Org. Lett.* **2010**, 240

# Zhang's group

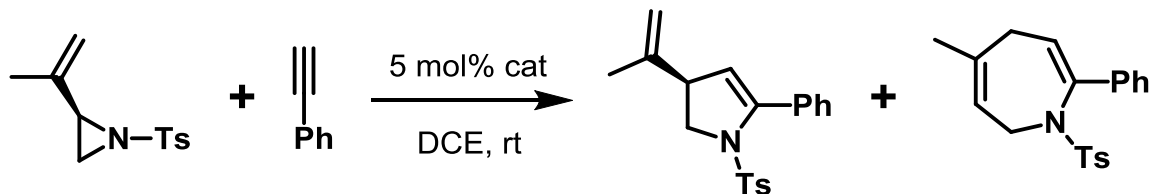


Zhang, *J. Am. Chem. Soc.* **2015**, 3787



Zhang, *Angew. Chem. Int. Ed.* **2015**, 15854

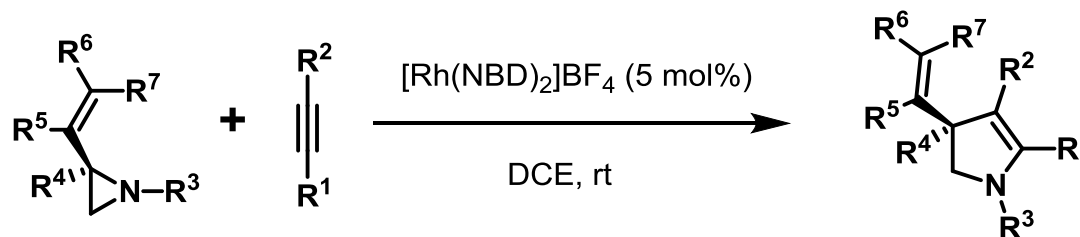
# Optimization



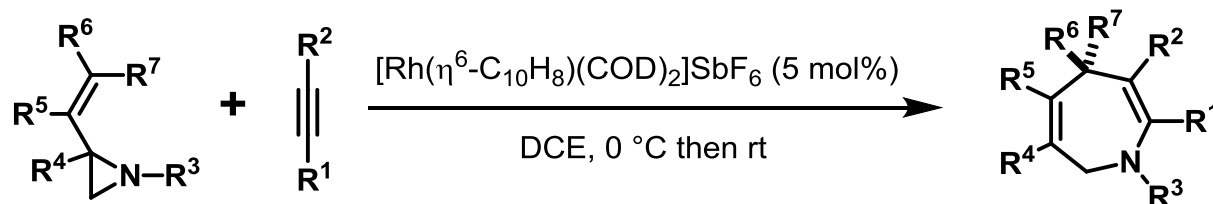
Entry	cat	Yield (%)	
		(3+2) (ee)	(5+2)
1	[Pd] cat	0	0
2	AgSbF <sub>6</sub>	-	-
3	FeCl <sub>3</sub>	-	-
4	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub>	0	0
5	[Rh(NBD) <sub>2</sub> ]BF <sub>4</sub>	90 (97)	0
6	[Rh(COD)Cl] <sub>2</sub> /AgSbF <sub>6</sub>	<10	85
7	[Rh(η <sup>6</sup> -C <sub>10</sub> H <sub>8</sub> )(COD)] SbF <sub>6</sub>	<5	91

# Optimized conditions

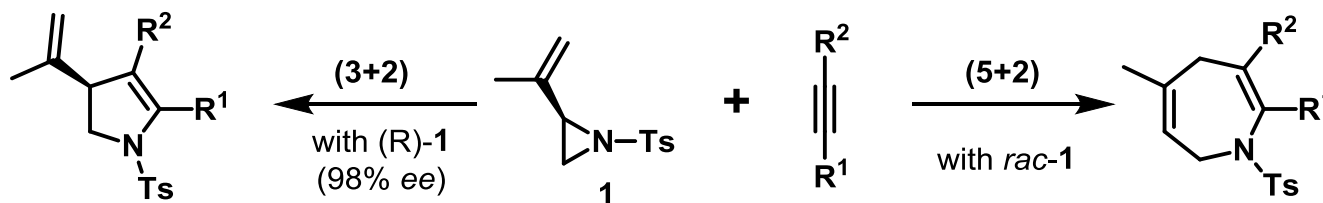
- Conditions for (3+2)



- Conditions for (5+2)



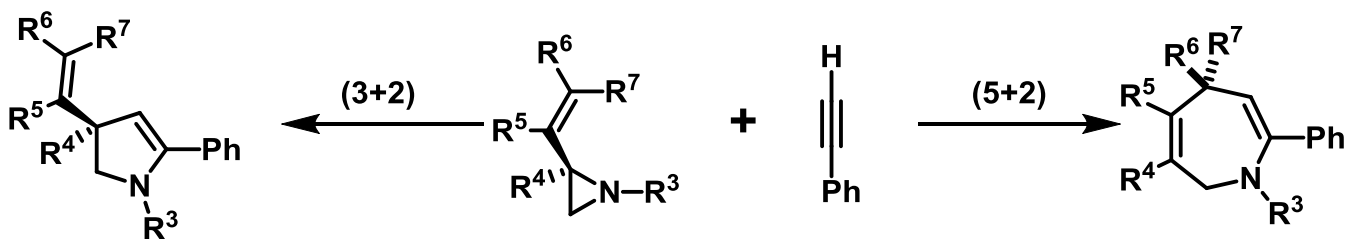
# Scope of alkyne

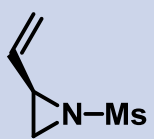
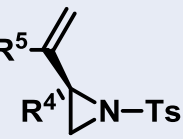
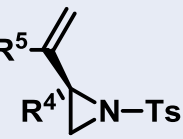
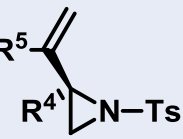
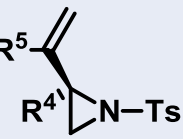
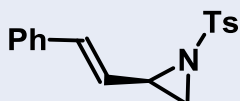


Entry	R <sup>1</sup> /R <sup>2</sup>	(3+2) yield (ee) (%)	(5+2) yield (%)
1	Ph/H	80 (97)	90
2	<i>n</i> -C <sub>3</sub> H <sub>7</sub> /H	90 (97)	90 <sup>a</sup>
3	(CH <sub>2</sub> ) <sub>3</sub> OBn/H	65 (97)	75 <sup>a</sup>
4	TMS/Me	64 (96)	40 of (3+2) adduct
5	Ph/COMe	75 (94)	37 of (3+2) adduct

<sup>a</sup>other regioisomer observed

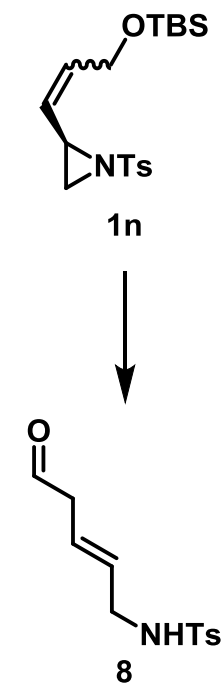
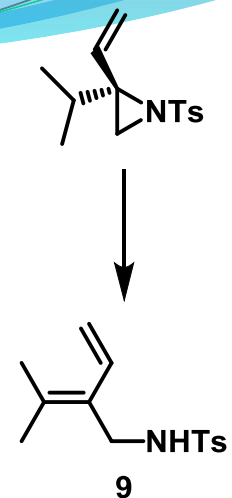
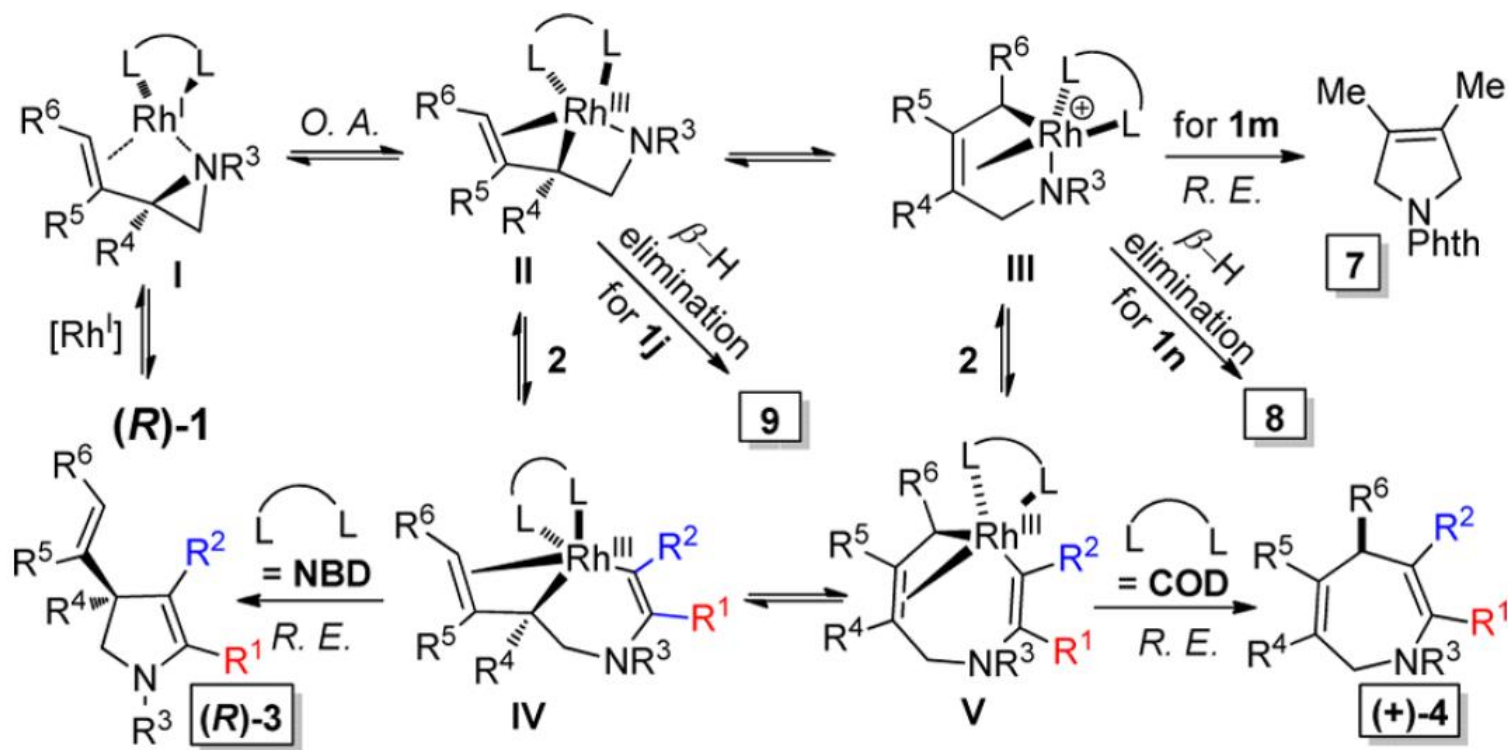
# Scope of vinylaziridine



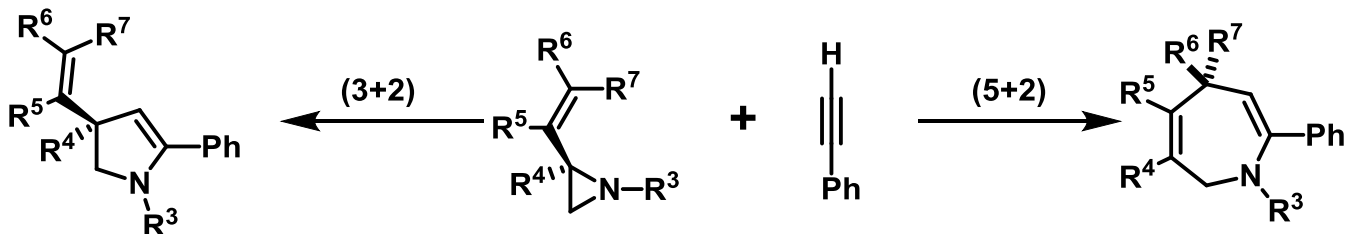
Entry	Aziridine (ee%)	[3+2] yield (ee) (%)	[5+2] yield (%)
1	 (86%)	50 (86%)	62
2	 R <sup>4</sup> = H, R <sup>5</sup> = iPr(90%)	72 (90)	92
3	 R <sup>4</sup> = H, R <sup>5</sup> = Ph(97%)	75 (99)	90
4	 R <sup>4</sup> = H, R <sup>5</sup> = OTBS(95%)	84 (95)	78
5	 R <sup>4</sup> = Me, R <sup>5</sup> = Me(86)	55 (85)	40
6	 (98)	53 (32)	40 (mixture of [3+2] and [5+2])



# Proposed mechanism



# Conclusion



- Switchable process
- General substrate
- Mild conditions



**Thank you  
for  
your attention**