镍和钴催化的烯基卡宾环加成反应

汇报人：施展
导师：陆平 研究员

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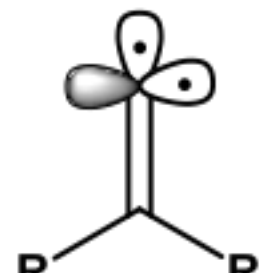
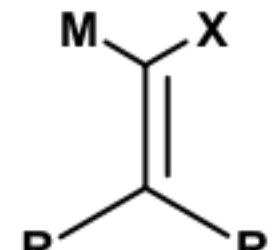
烯基卡宾的结构

单线态



三线态



金属烯基卤化物

单线态比三线态能量低48 kcal/mol
因此更稳定

Carter, E. A. *J. Phys. Chem.* **1991**, *95*, 8352-8363.

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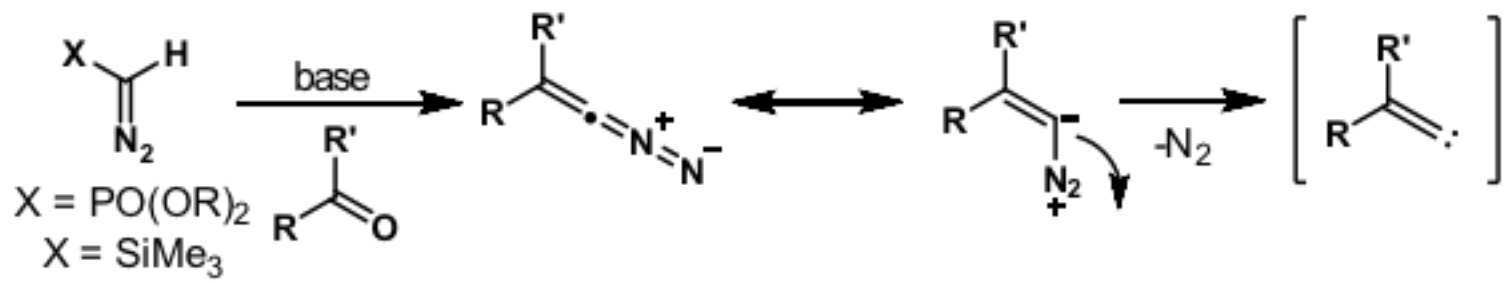
烯基卡宾的生成

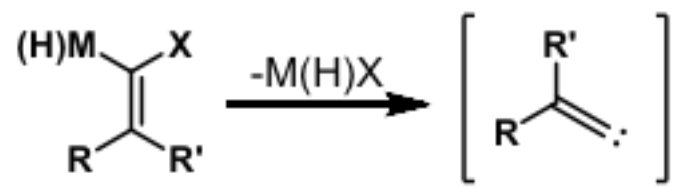
1. 烯基偶氮化合物释放氮气



Thomas, R. *Chem. Rev*. **1974**, *74*, 87-99.

Moritani, T. *J. Chem. Soc., Chem. Commun.* **1992**, 721-722.

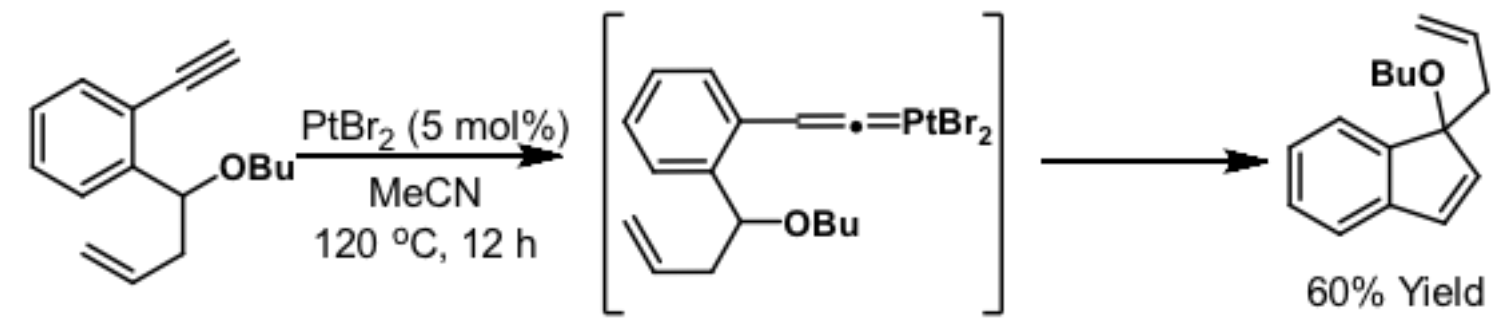
2. 乙烯基卤化物的消除



Kirmse, W. *Angew. Chem., Int. Ed.* **1965**, *4*, 1-10.

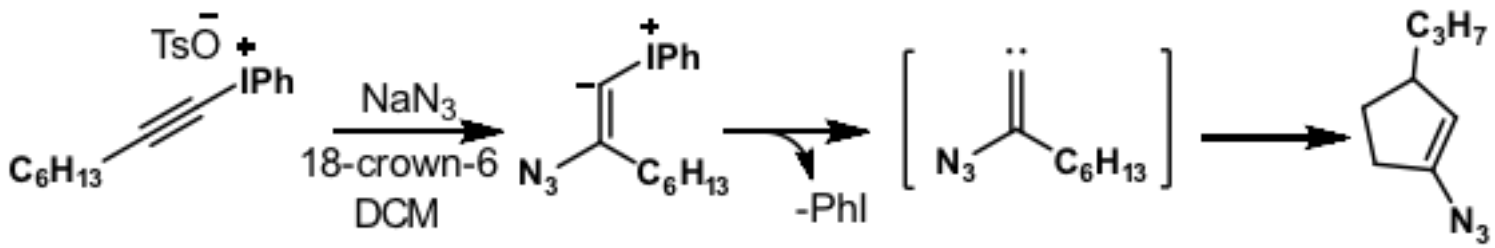
烯基卡宾的生成

3. 金属烯基卡宾



Yamamoto, Y. *J. Org. Chem*. **2006**, *71*, 6204-6210.

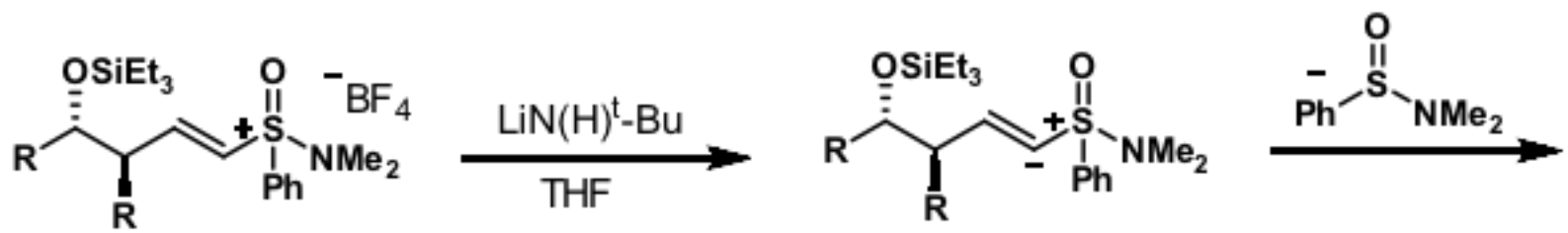
4. 高价碘化物生成烯基卡宾

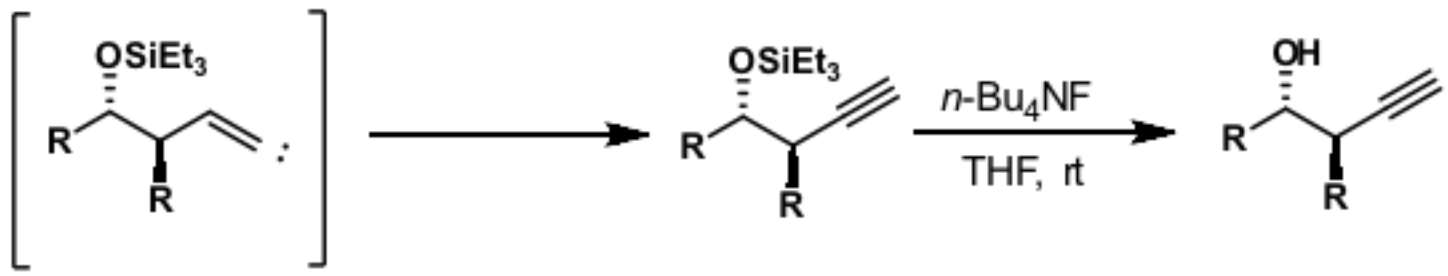


Stang, P. J. *Tetrahedron Lett.* **1988**, *29*, 1887-1890.

烯基卡宾的生成

5.乙烯基氨基磺铵盐生成烯基卡宾





Raabe, G. *J. Am. Chem. Soc*. **2002**, *124*, 10427-10434

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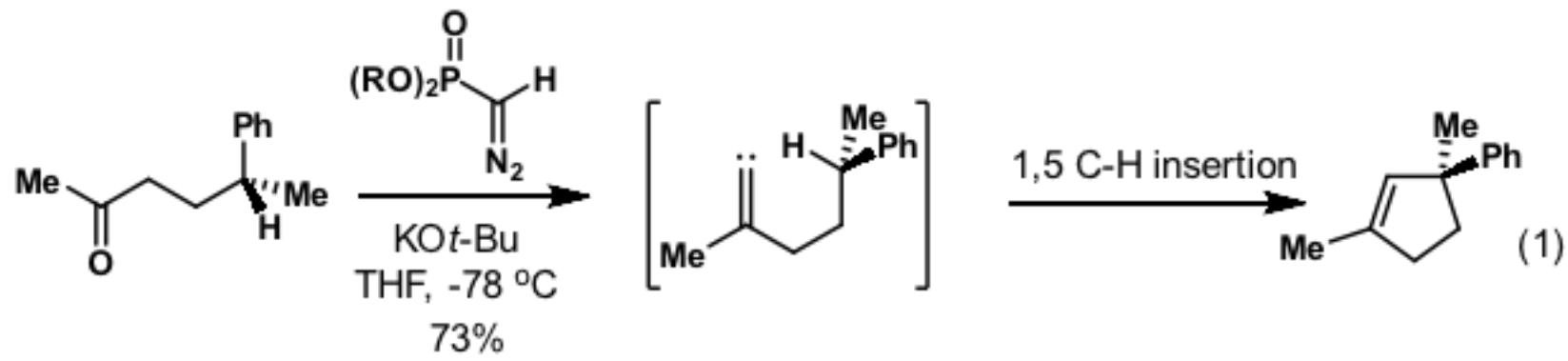
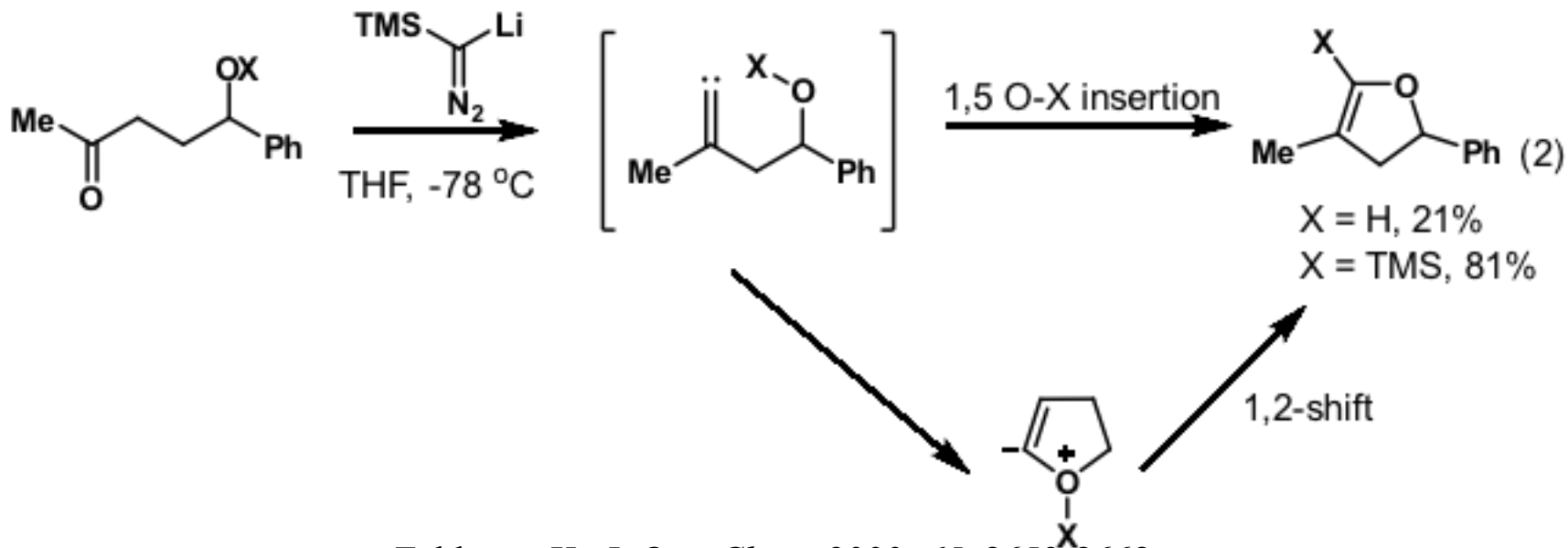
烯基卡宾参与的反应

1. 1,5 C-H键插入反应



Gilbert, J. *J. Org. Chem*. **1985**, *50*, 2557-2563

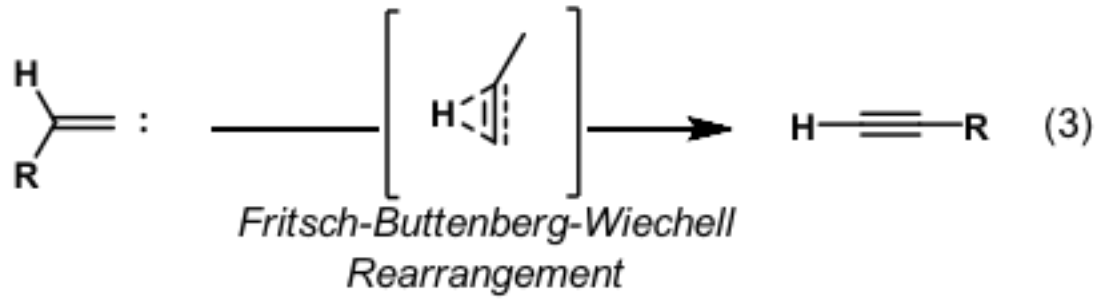
2. 1,5 O-X键插入反应



Feldman, K. *J. Org. Chem*. **2000**, *65*, 8659-8668.

烯基卡宾参与的反应

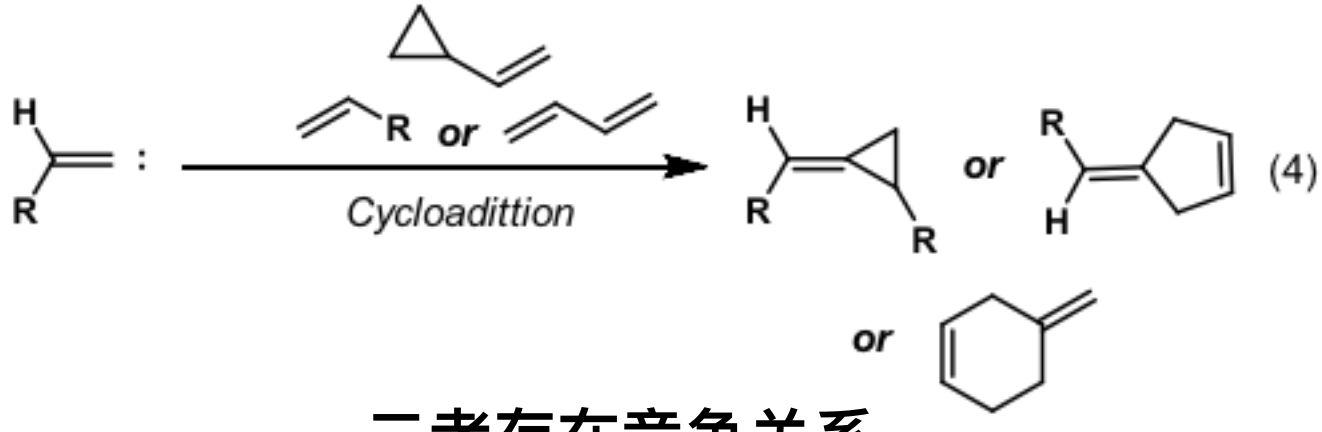
3. FBW重排反应



Chang, N. *J. Chem. Phys.* **1997**, *106*, 3237-3242

当烯基卡宾的*β*-位有H时，重排经过的能垒仅需1.5 kcal/mol

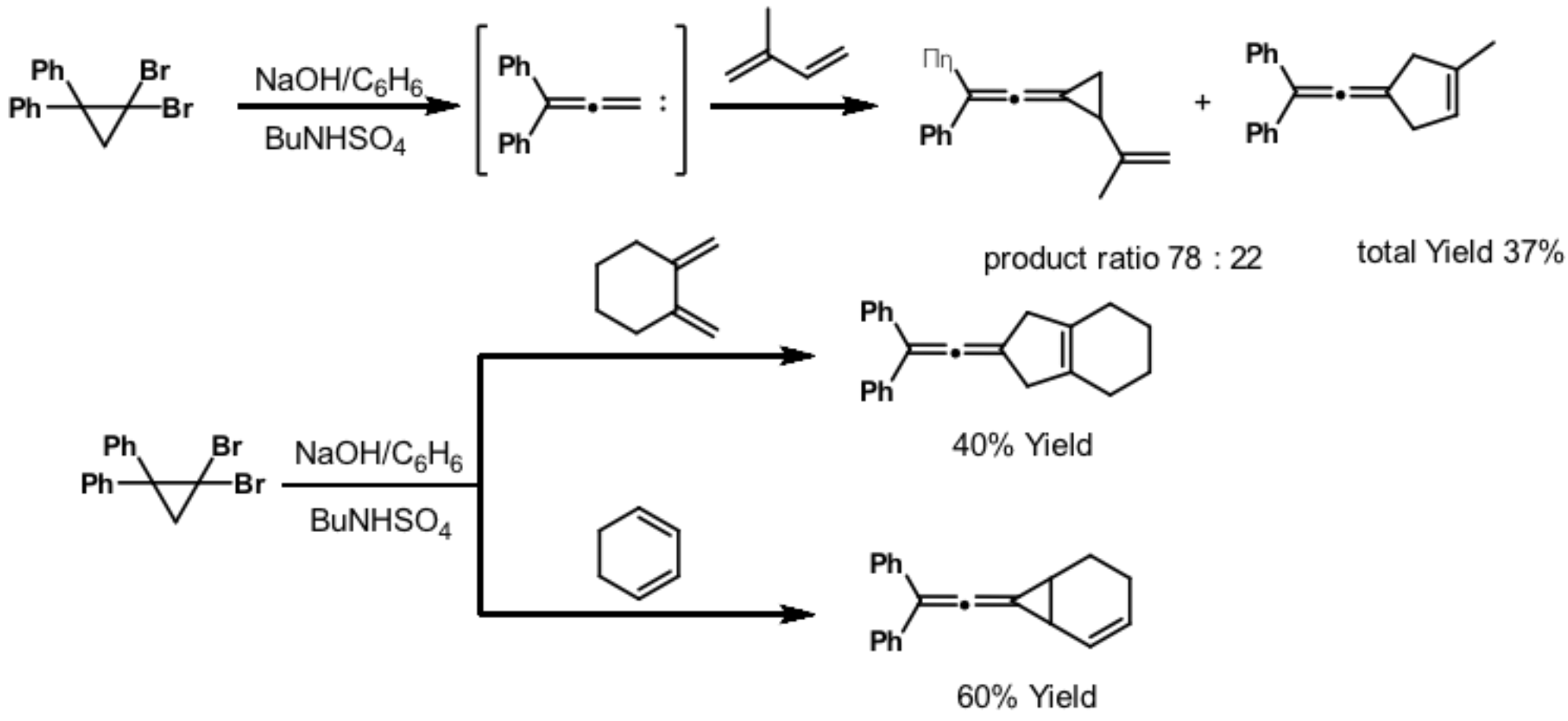
4. 环加成反应



二者存在竞争关系

烯基卡宾参与的反应

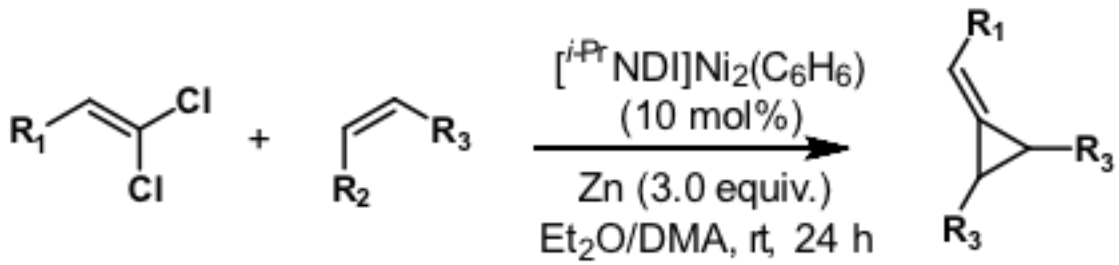
首例烯基卡宾的[4+1]和[2+1]反应

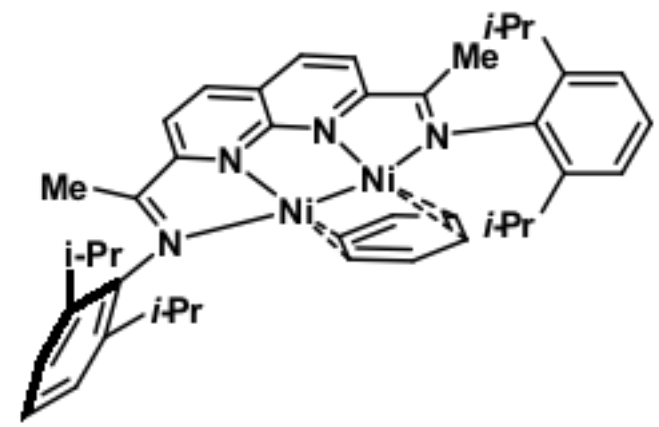


Otsuji, Y., *Angew. Chem., Int. Ed.,* **1991**, *30*, 984-986.

烯基卡宾参与的反应

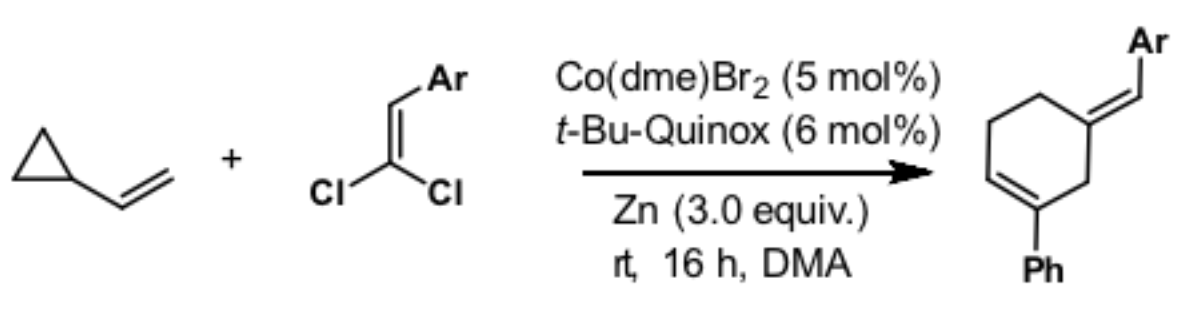
双核镍催化的烯基卡宾[2+1]环加成反应

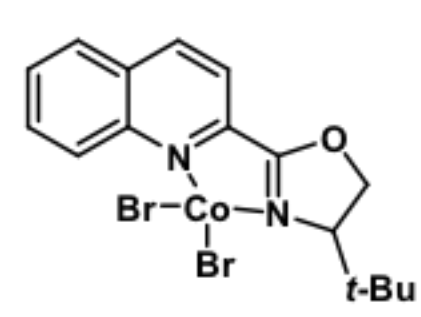




Uyeda, C *J. Am. Chem. Soc.* **2017**, *139*, 11686−11689

钴催化的烯基卡宾[5+1]环加成反应

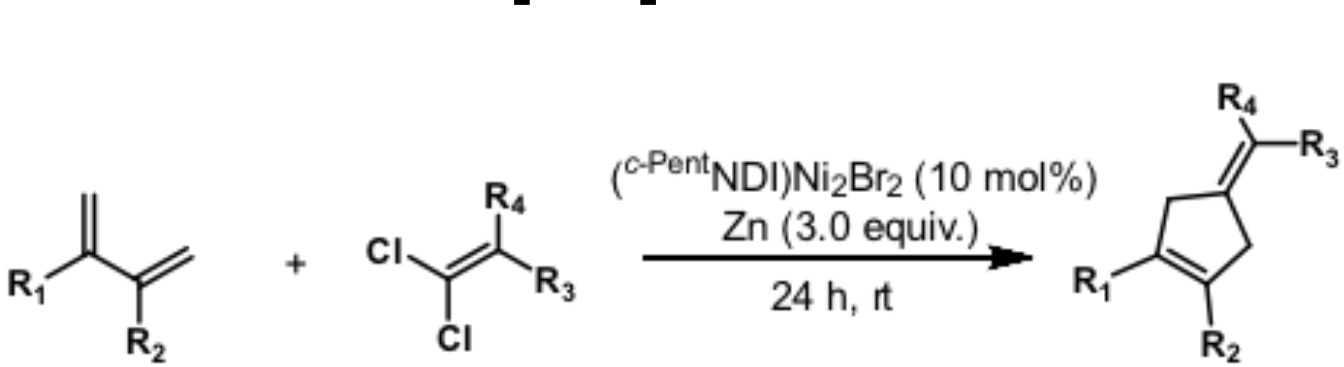


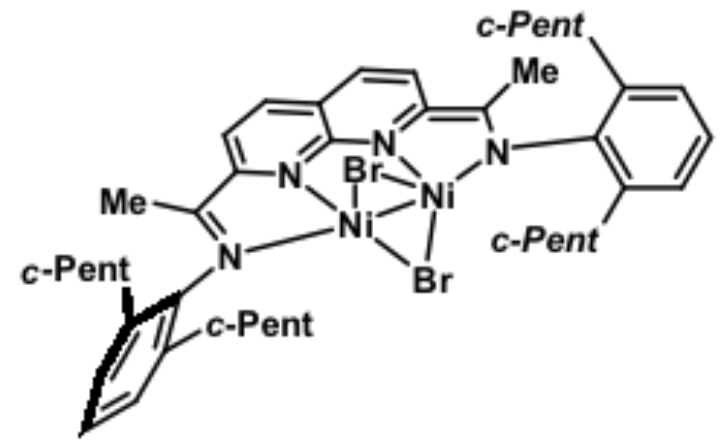


Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 4598−4603

烯基卡宾参与的反应

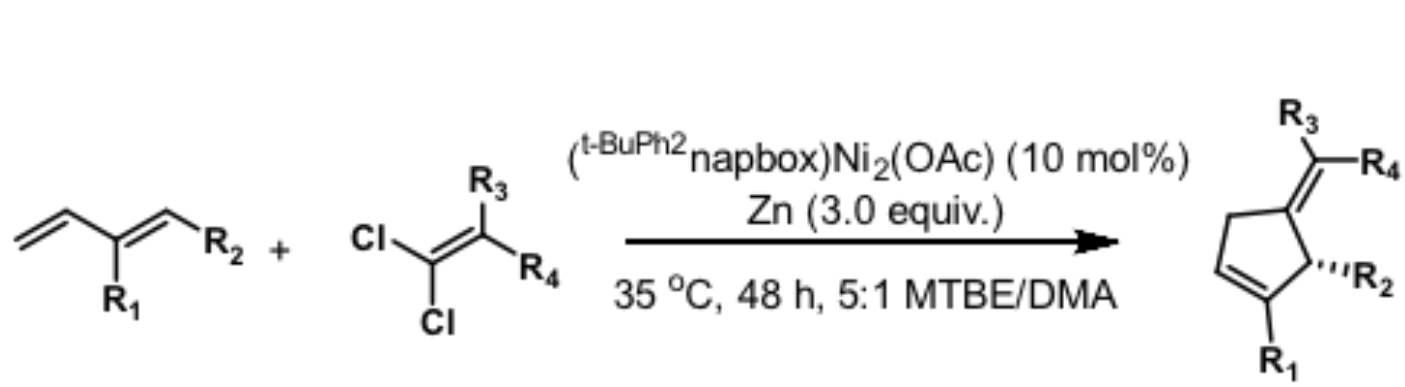
双核镍催化的烯基卡宾[4+1]环加成反应

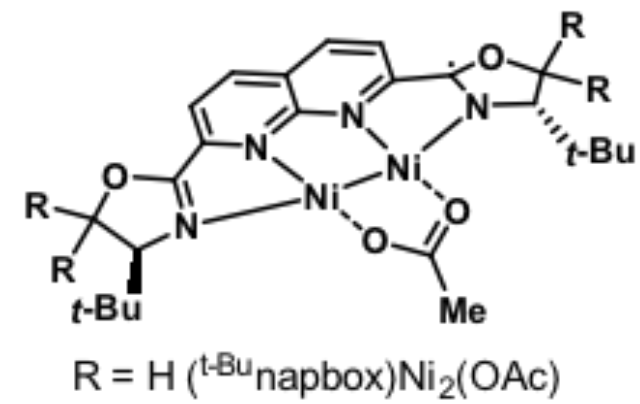




Uyeda, C., *Science*, **2019**, *363*, 857-862

手性双核镍催化的烯基卡宾[4+1]环加成反应





Uyeda, C., *J. Am. Chem. Soc.*, **2020**, *142*, 17294-17300

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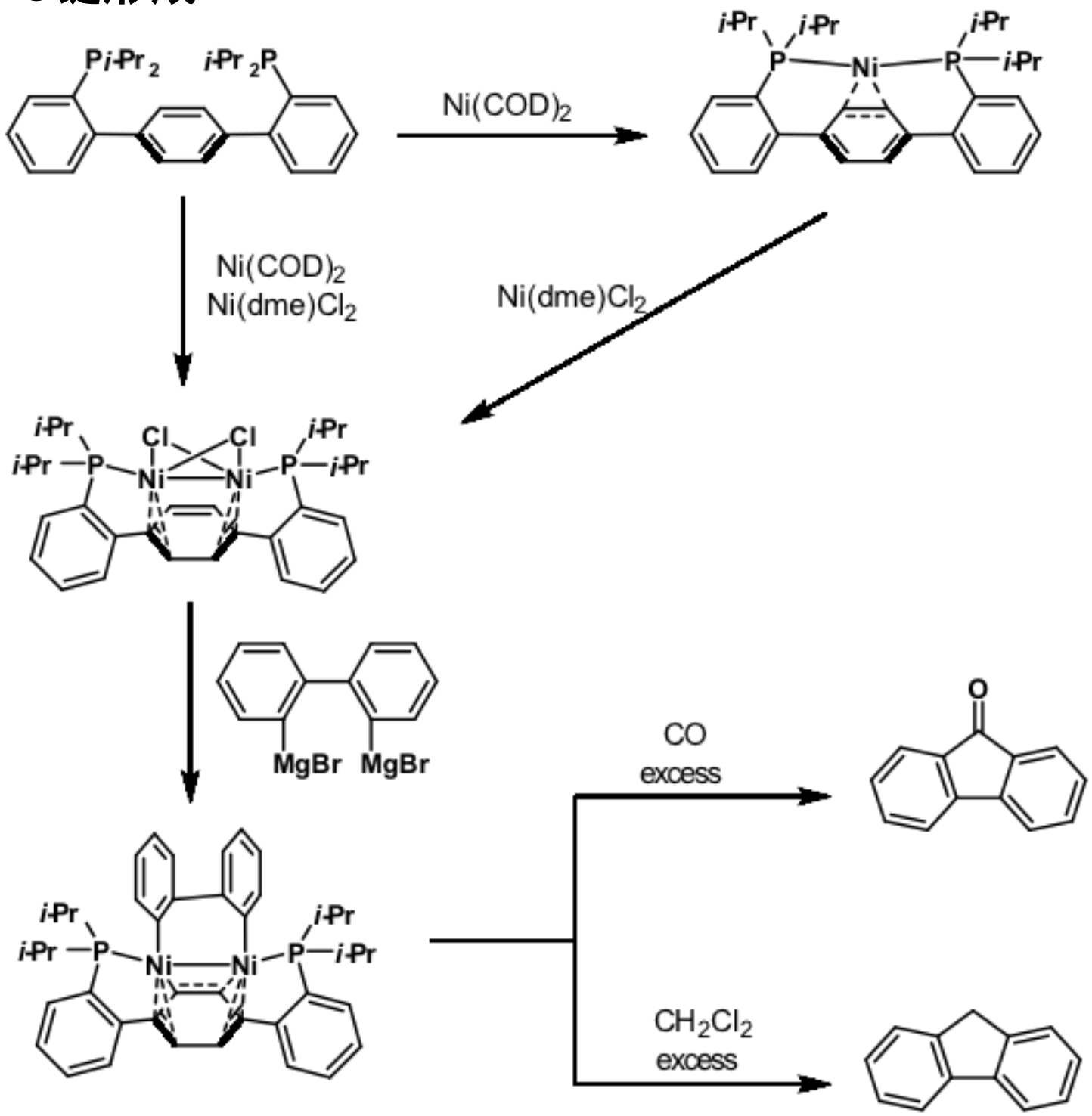
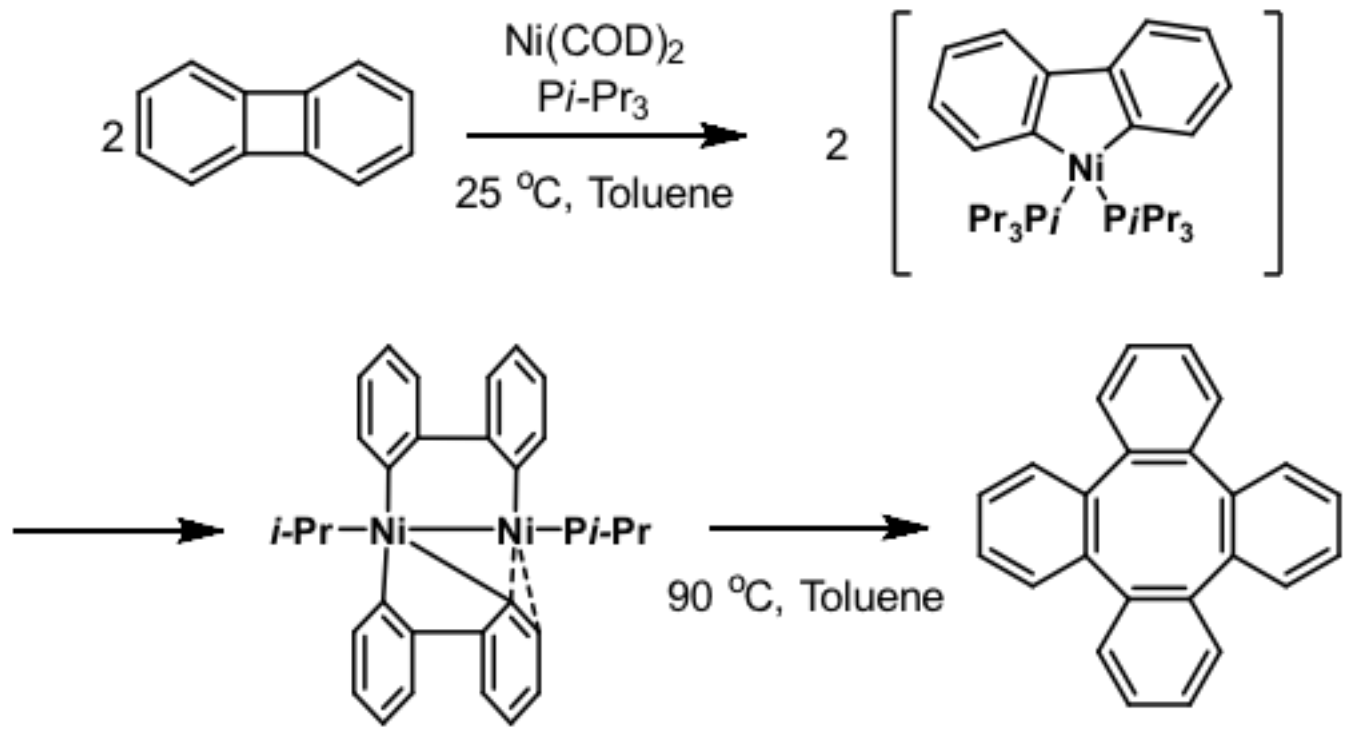
双核镍催化剂简介

双核镍介导的C-C键形成



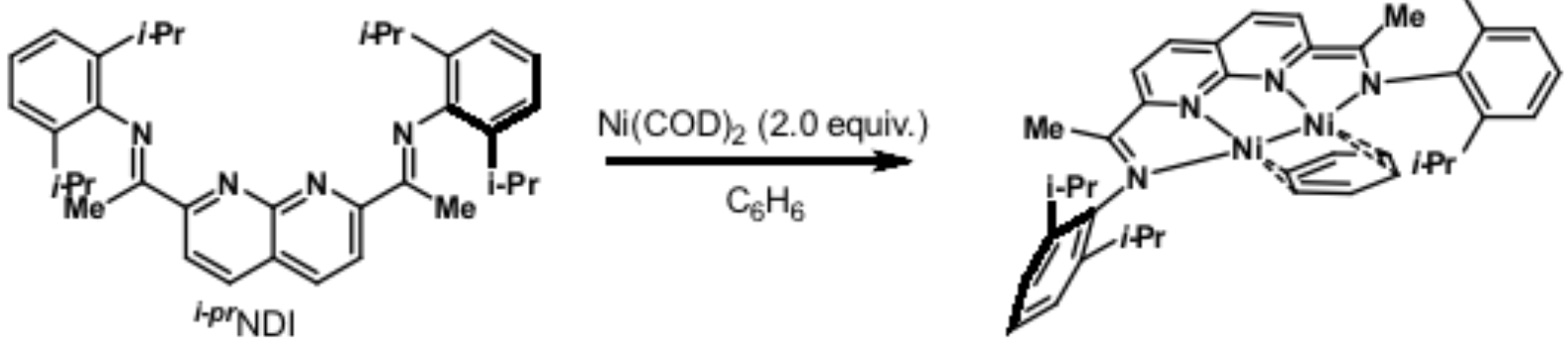
Theodor A., *J. Am. Chem. Soc.,* **2010**, *132*, 6296-6297.

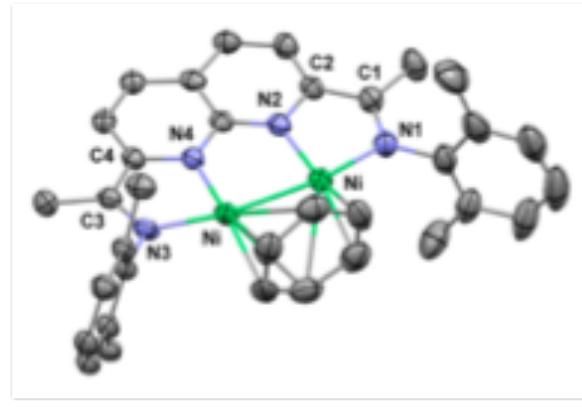
双核镍催化剂简介



Samuel A. J., *Chem. Commun,* **2011**, *47*, 9233-9235

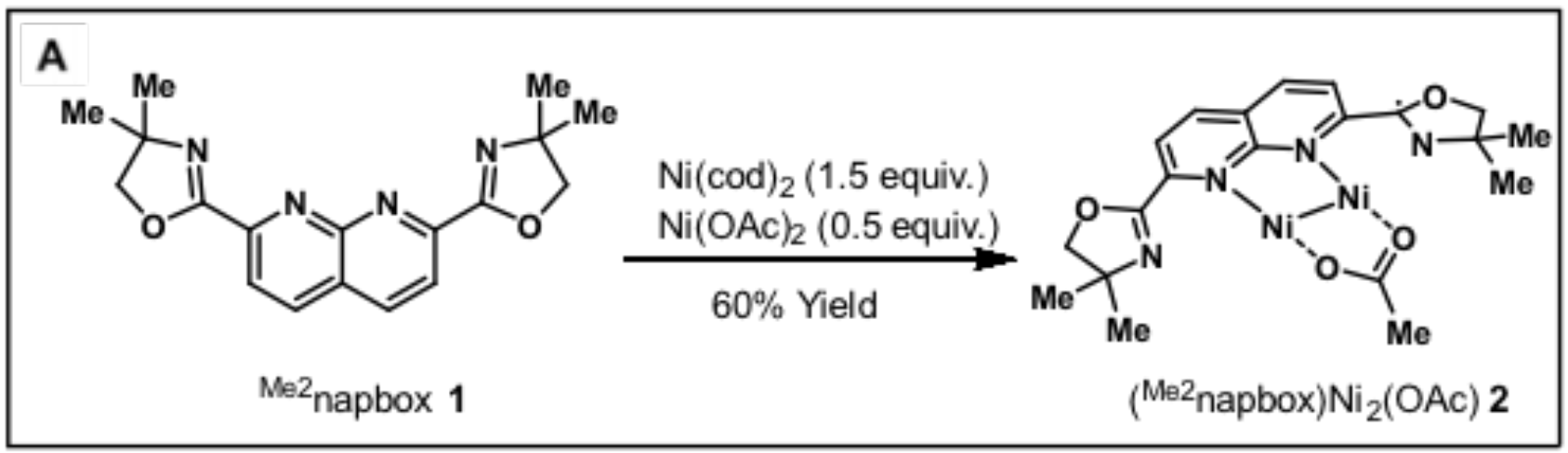
双核镍催化剂的合成

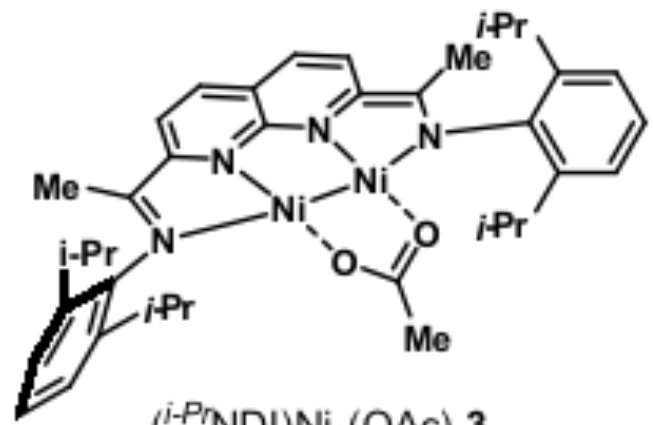




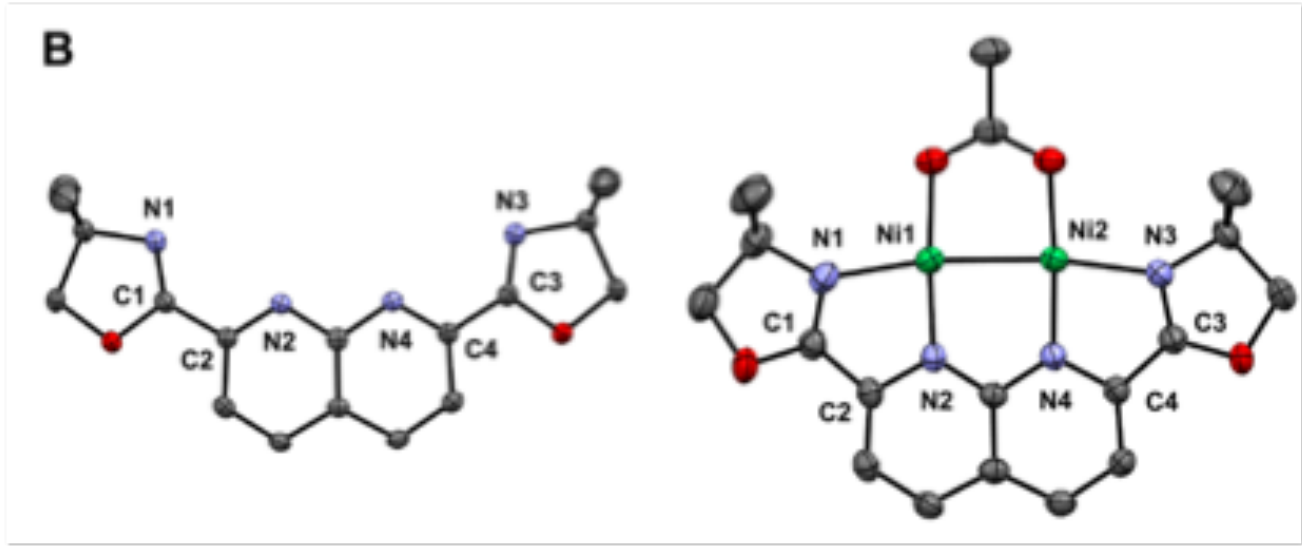
Uyeda, C., *Inorg. Chem.*, **2014**, *53*, 11770-11777.

双核镍催化剂简介





双核镍催化剂的单晶结构



	Me2napbox 1	(Me2napbox)Ni2(OAc) 2
Ni1-Ni1	/	2.372(1) Å
N1-C1	1.261(5) Å	1.282(5) Å
C1-C2	1.479(4) Å	1.436(6) Å
N2-C2	1.329(4) Å	1.379(5) Å
N3-C3	1.261(5) Å	1.282(5) Å
C3-C4	1.479(4) Å	1.439(5) Å
N4-C4	1.329(4) Å	2.372(1) Å

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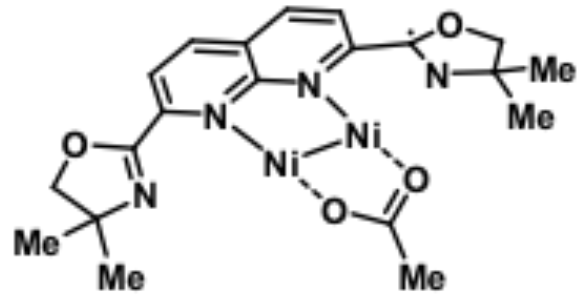
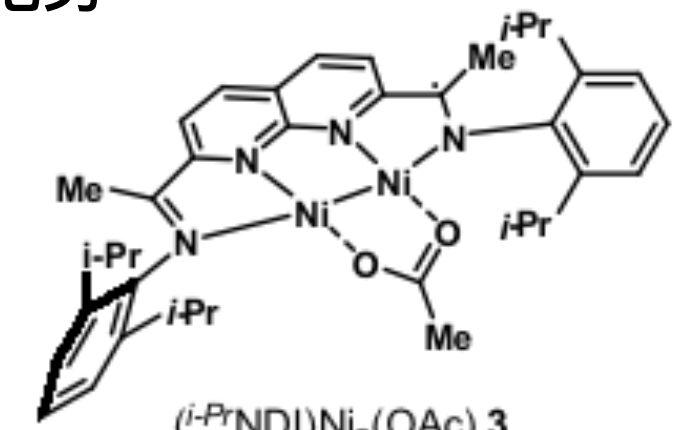
双核镍催化剂简介

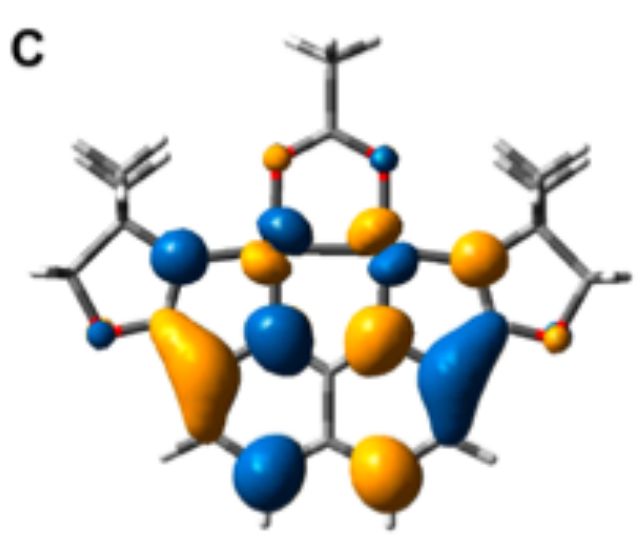
双核镍催化剂的SOMO计算，EPR光谱及电势



(^{Me2}napbox)Ni_2(OAc) **2**

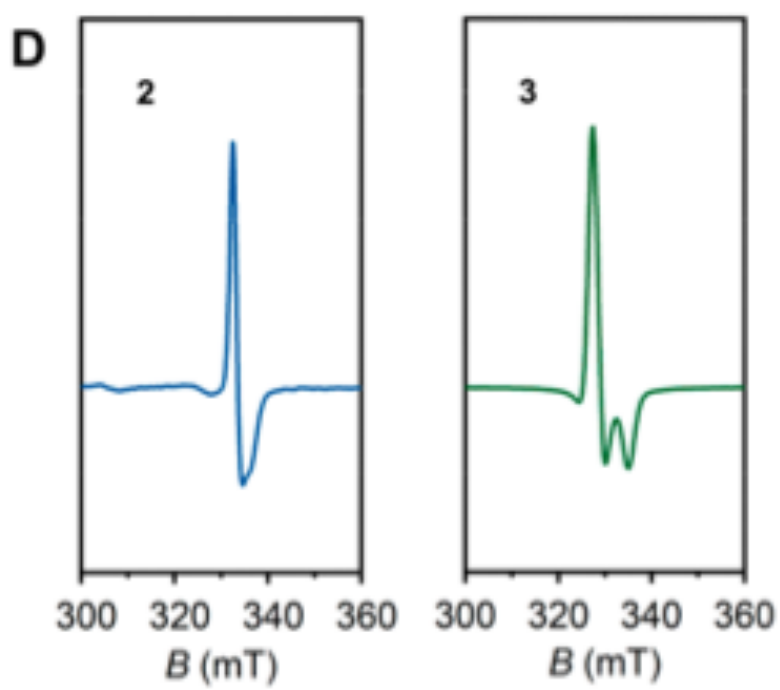


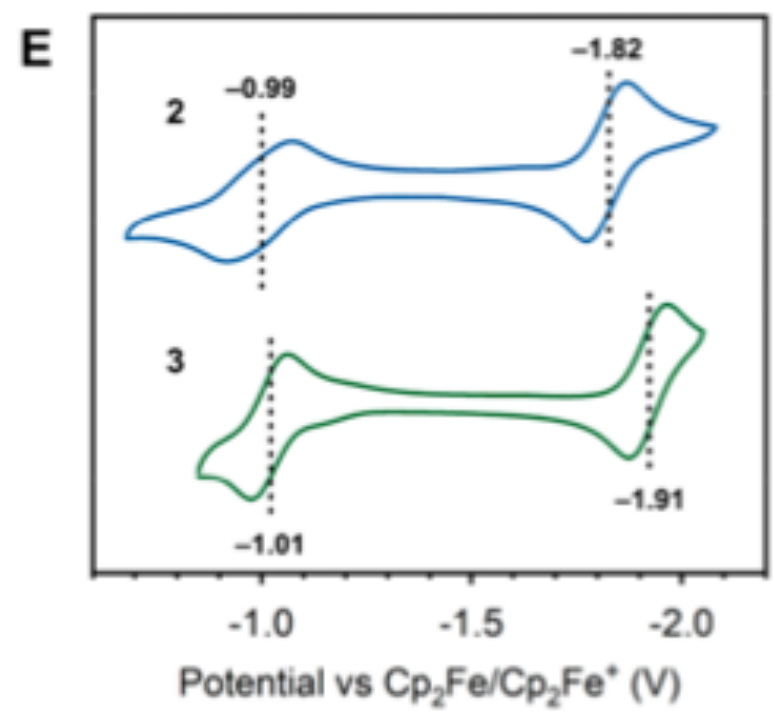
($^{i\text{-}Pr}$NDI)Ni_2(OAc) **3**



(^{Me2}napbox)Ni_2(OAc) (**2**)

SOMO





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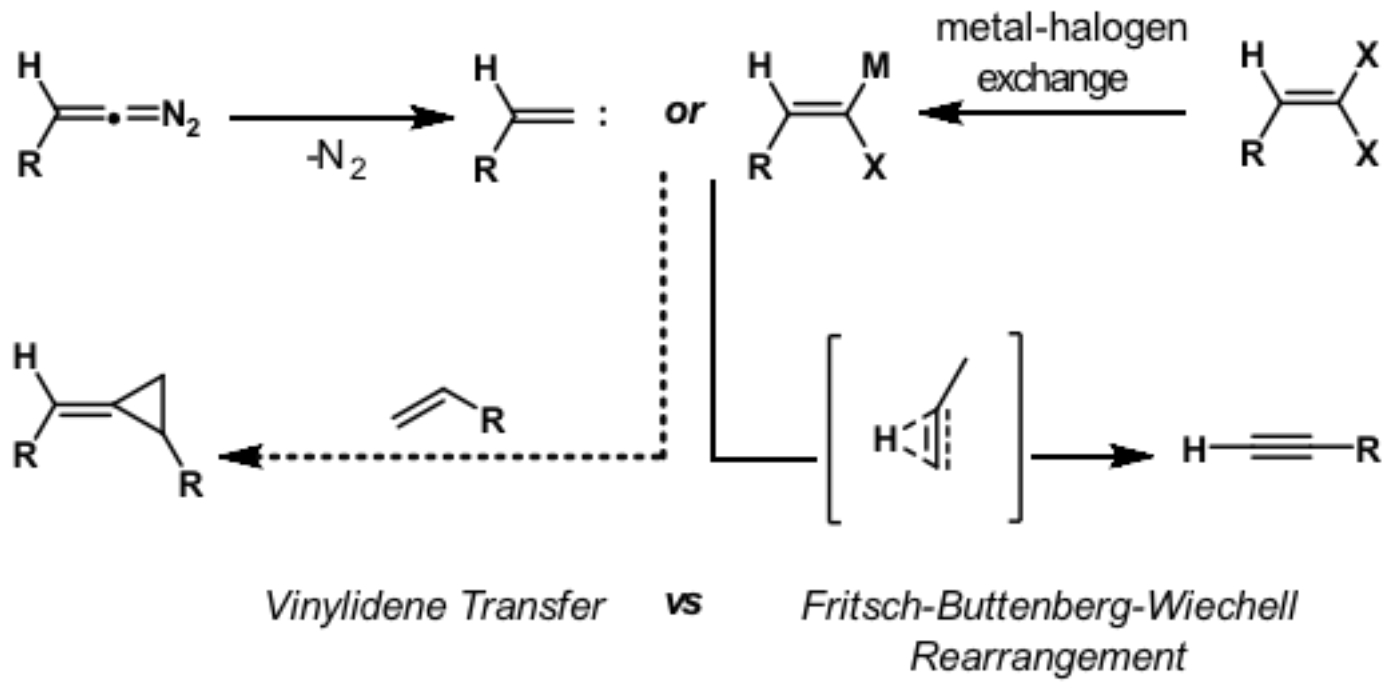
双核镍催化的烯基卡宾的[2+1]环加成反应

烯基卡宾的迁移与FBW重排互相竞争



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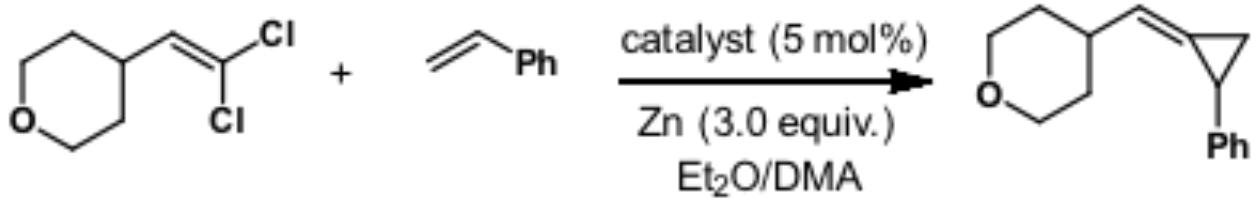
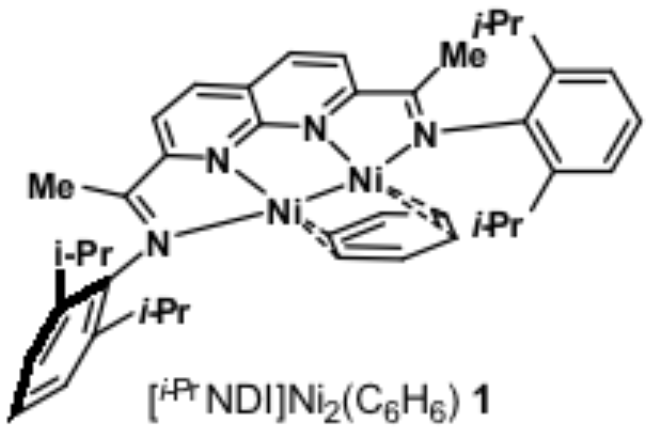
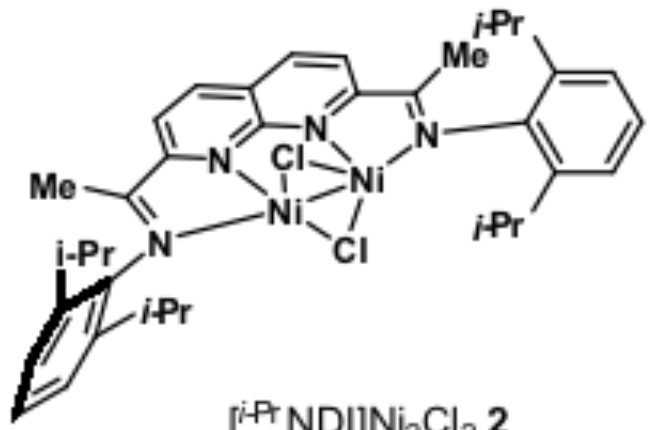
双核镍催化的烯基卡宾的[2+1]环加成反应

◆ 配体筛选：

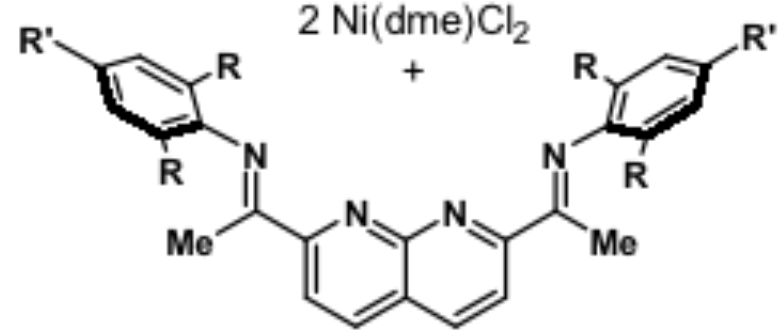




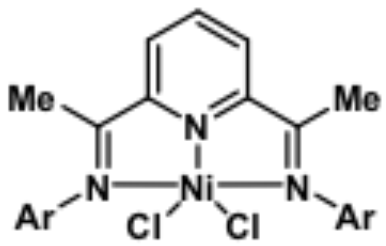
[$^{i\text{-Pr}}$NDI]$Ni_2(C_6H_6)$ **1**
94% Yield *E*/*Z* = 1:5



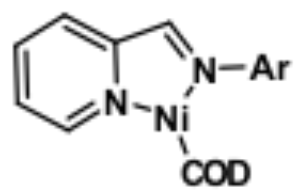
[$^{i\text{-Pr}}$NDI]Ni_2Cl_2 **2**
87% Yield *E*/*Z* = 1:5



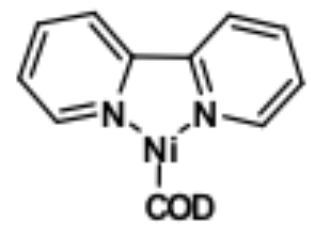
R = *i*-Pr , R' = H **3** 92% Yield *E*/*Z* = 1:5
R = Et , R' = H **4** 50% Yield *E*/*Z* = 1:1
R = R' = Me **5** <2% Yield



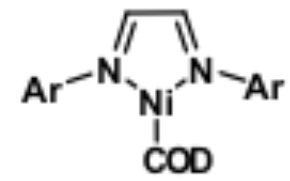
$^{i\text{-Pr}}$PDI]Ni_2Cl_2 **6**
<2% Yield



[$^{i\text{-Pr}}$IP]]Ni(COD) **7**
<2% Yield



[BPY]Ni(COD) **8**
<2% Yield

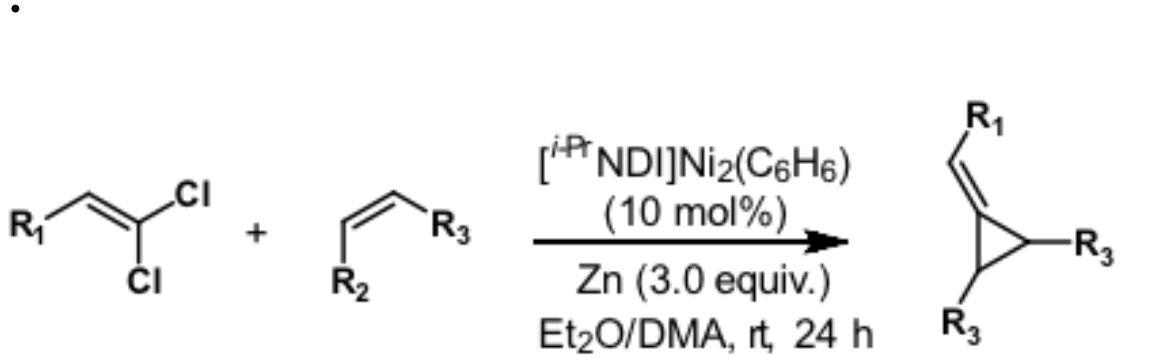


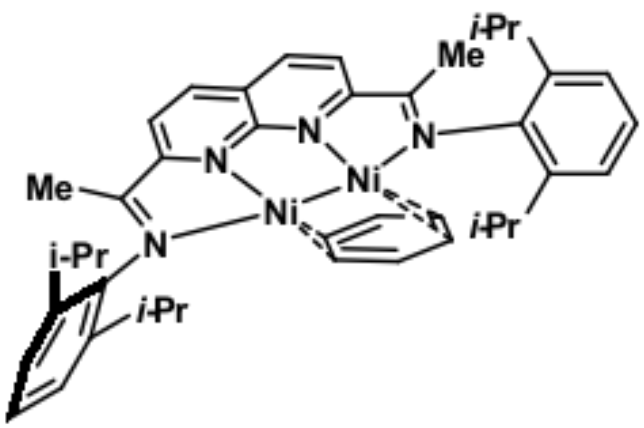
[$^{i\text{-Pr}}$DAD]Ni(COD) **9**
<2% Yield

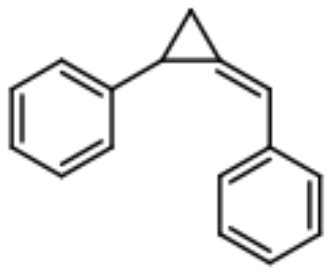
Uyeda, C *J. Am. Chem. Soc.* **2017**, *139*, 11686−11689

双核镍催化的烯基卡宾的[2+1]环加成反应

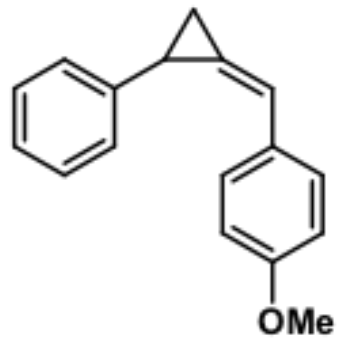
◆ 底物：



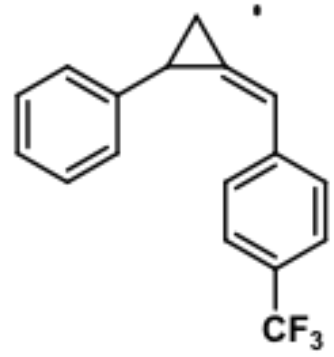




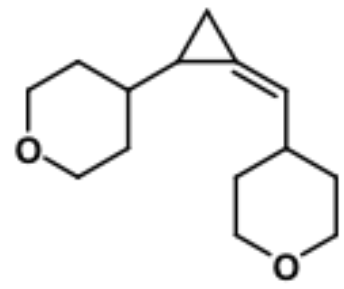
87% Yield
(*E*/*Z*) = 1:3



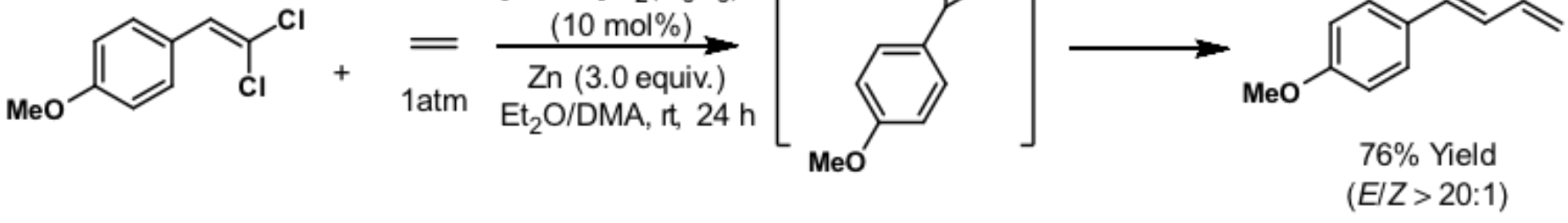
93% Yield
(*E*/*Z*) = 1:4



71% Yield
(*E*/*Z*) = 1:4



72% Yield
(*E*/*Z*) = 13:1



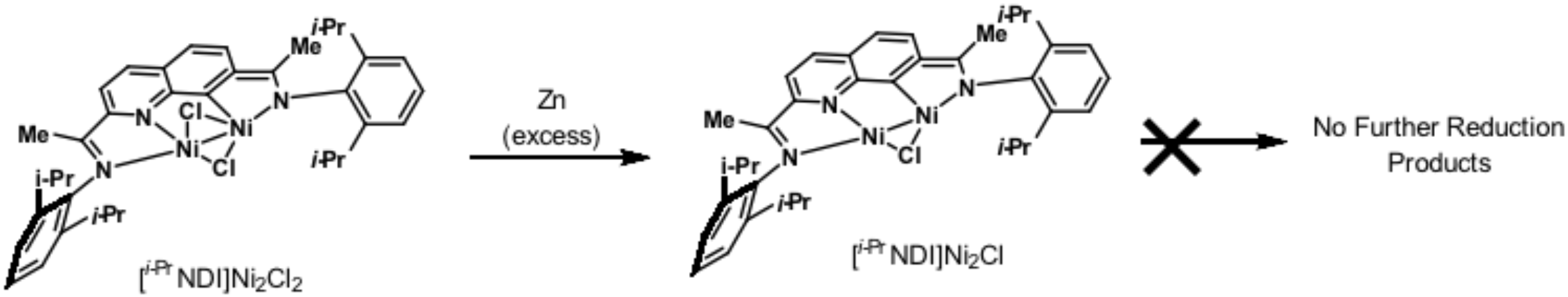
76% Yield
(*E*/*Z* > 20:1)

Uyeda, C *J. Am. Chem. Soc.* **2017**, *139*, 11686−11689

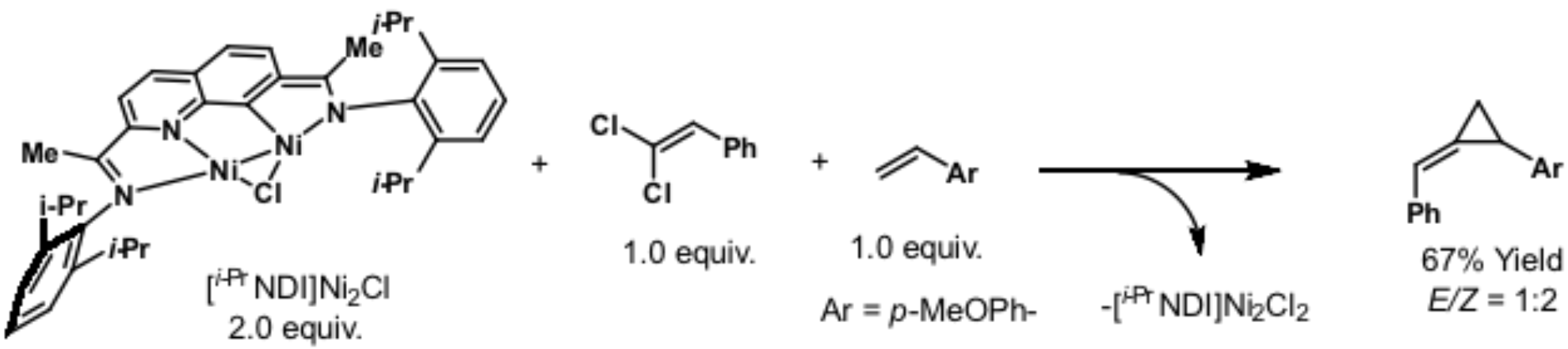
双核镍催化的烯基卡宾的[2+1]环加成反应

◆ **机理实验：**

1. Zn对Ni催化剂进行单电子还原



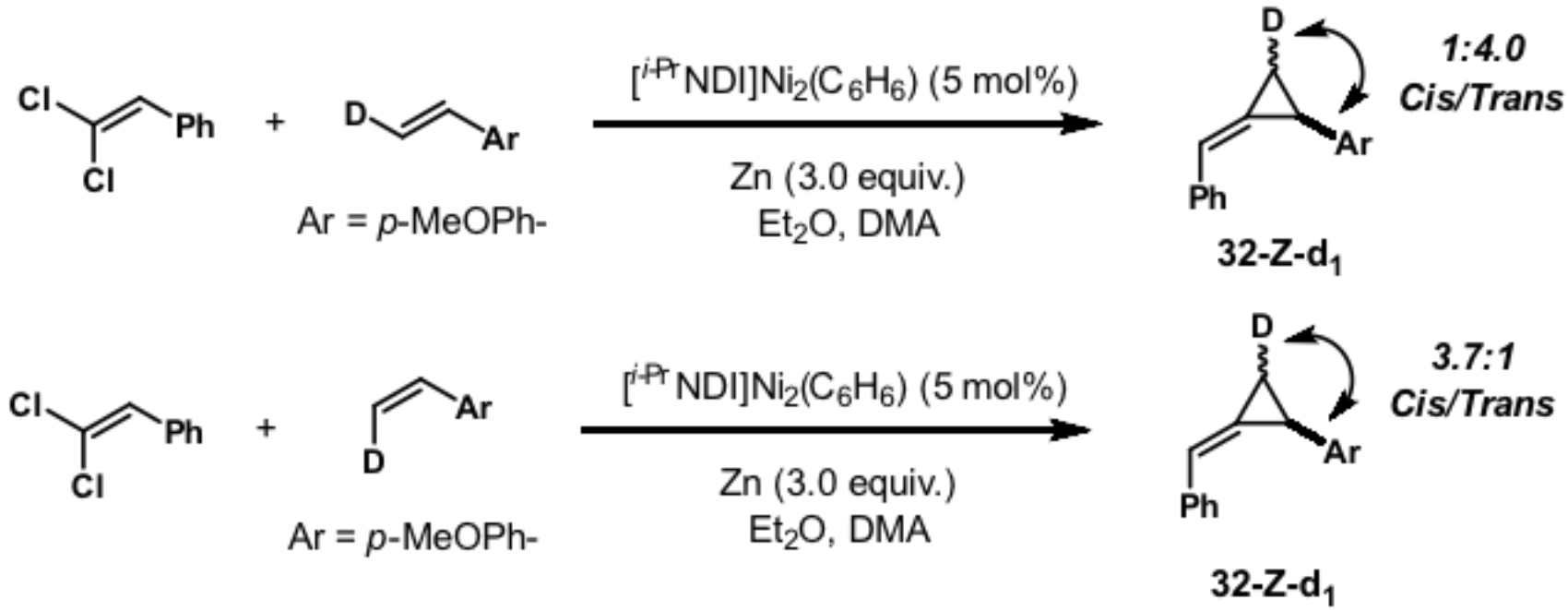
2. Zn在环丙烷化的过程是不必要的



Uyeda, C *J. Am. Chem. Soc.* **2017**, *139*, 11686−11689

双核镍催化的烯基卡宾的[2+1]环加成反应

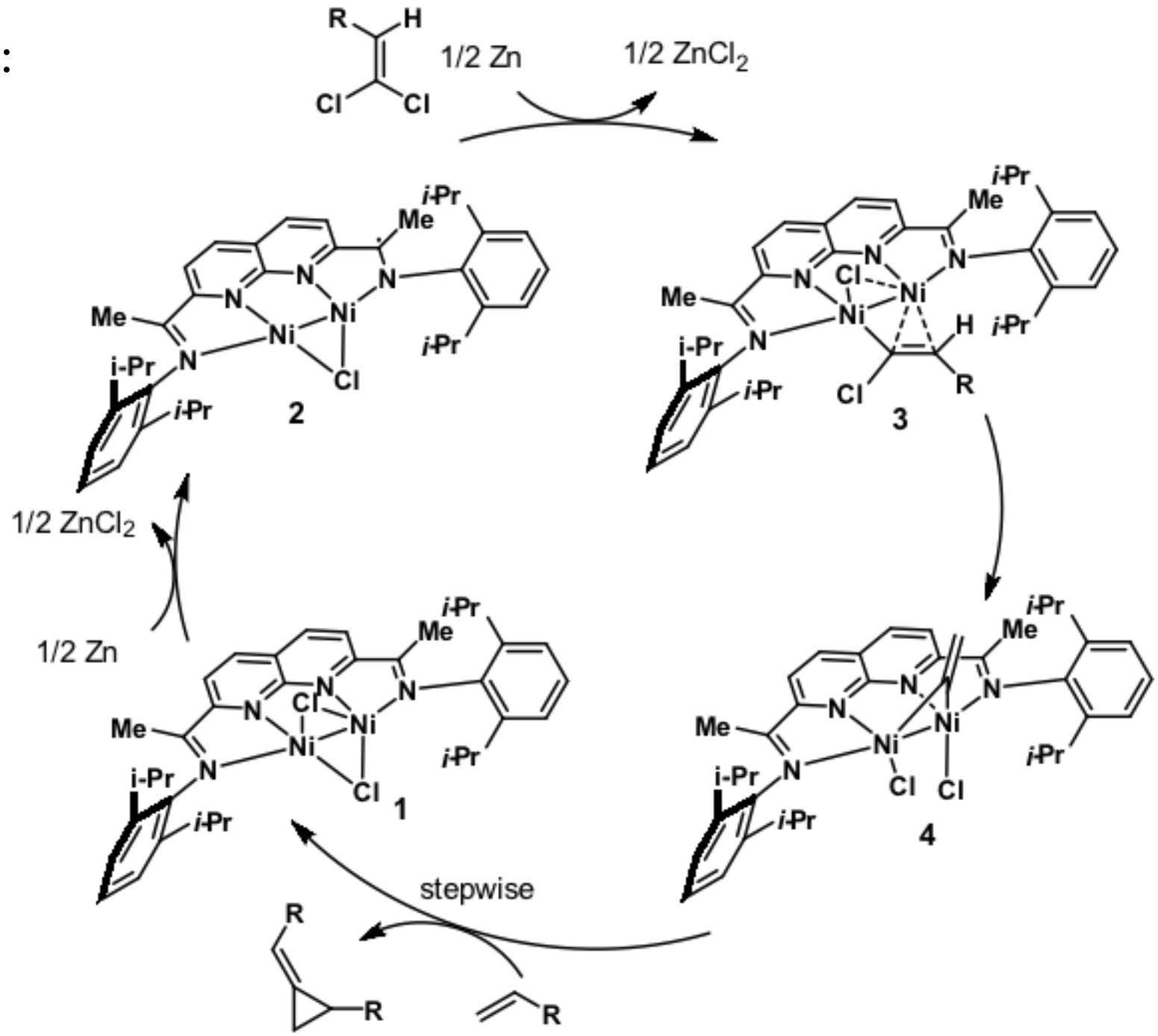
3. 环丙烷化的过程是分步的



Uyeda, C *J. Am. Chem. Soc.* **2017**, *139*, 11686−11689

双核镍催化的烯基卡宾的[2+1]环加成反应

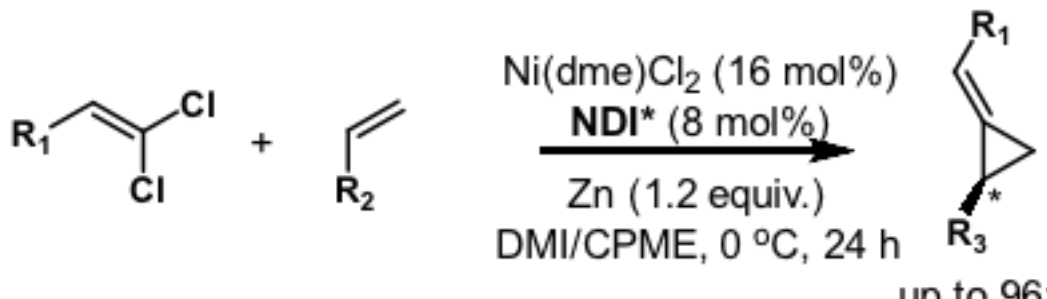
◆ 反应机理：

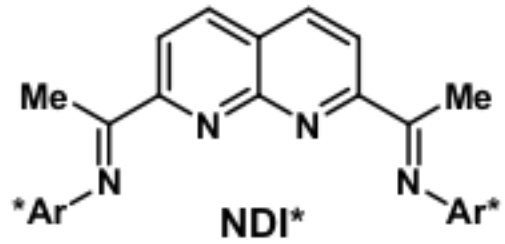


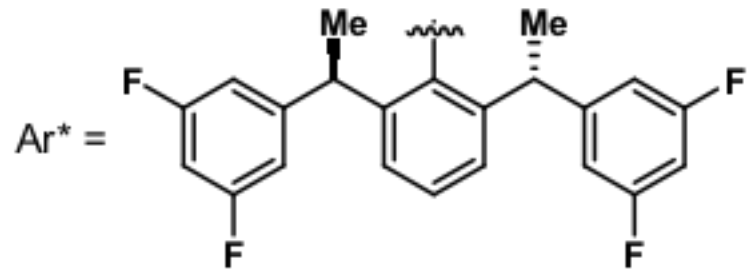
Uyeda, C *J. Am. Chem. Soc.* **2017**, *139*, 11686−11689

双核镍催化的烯基卡宾的[2+1]环加成反应

手性NDI双核镍催化的[2+1]反应



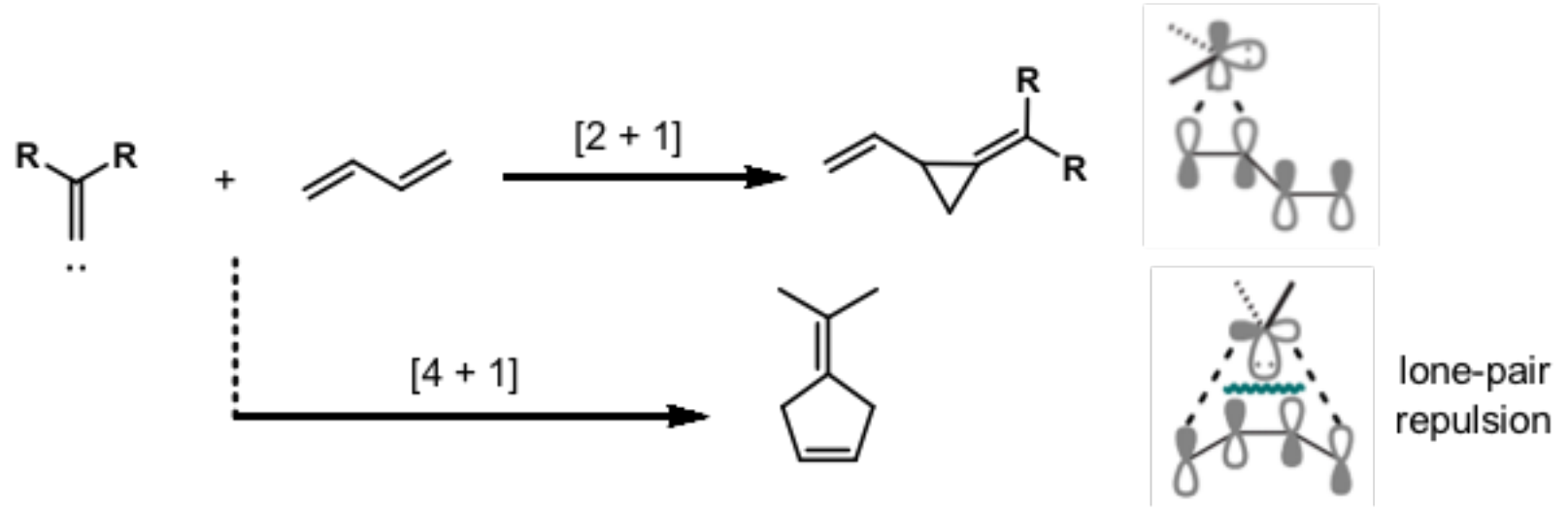




Cramer, N., *Angew. Chem. Int. Ed*., **2020**, *59*, 16425 -16429

双核镍催化的烯基卡宾的[4+1]环加成反应

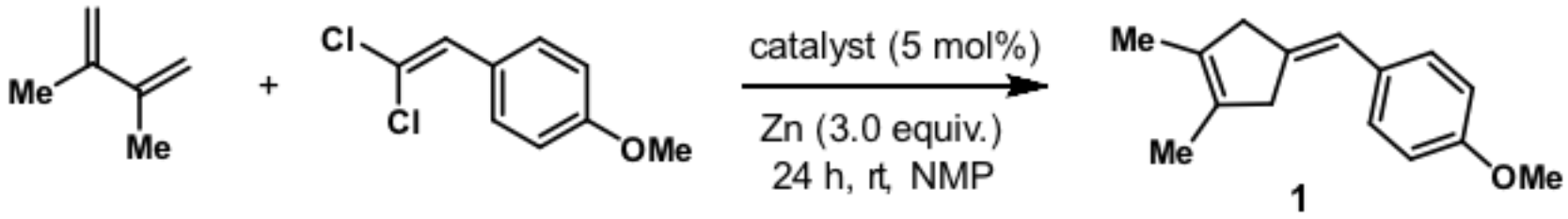
烯基卡宾发生[4+1]环加成的挑战



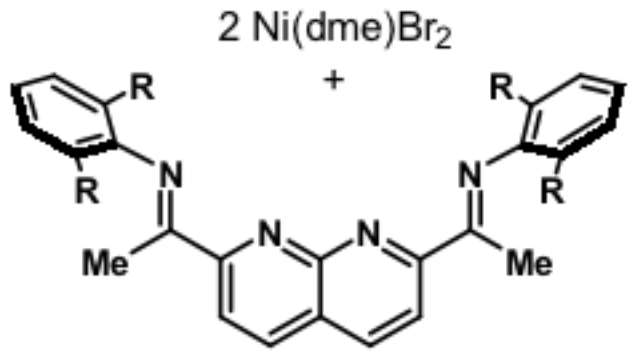
Uyeda, C., *Science*, **2019**, *363*, 857-862.

双核镍催化的烯基卡宾的[4+1]环加成反应

◆ 配体筛选：

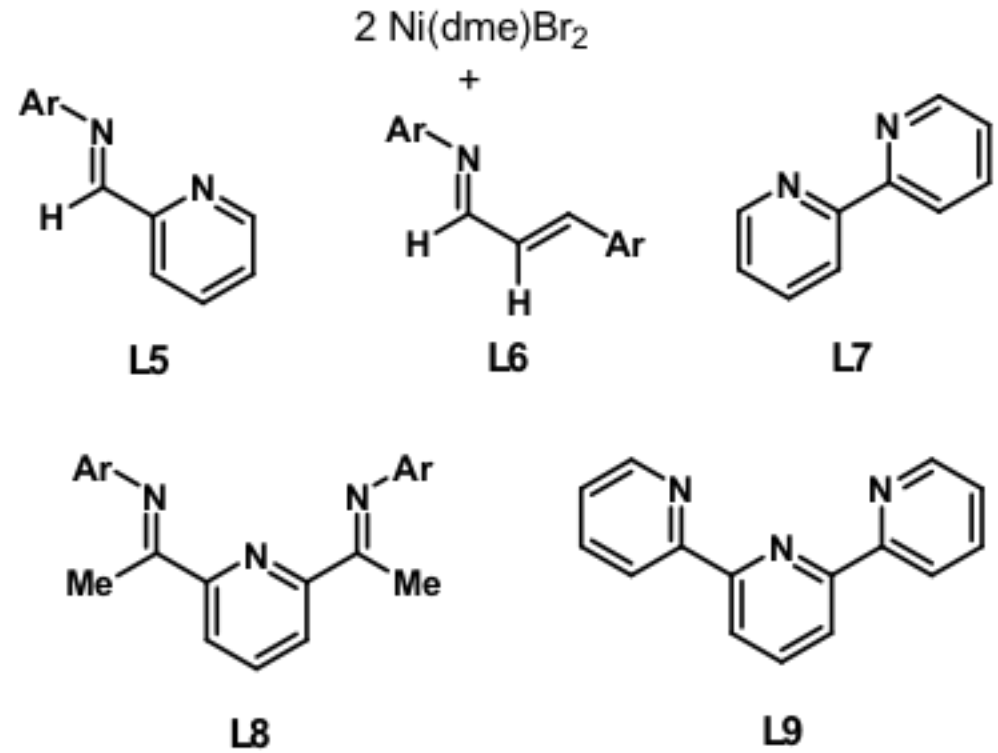


Binucleating Ligands



Steric Hindrance of Catalyst		Yield **1**
⇩	R = Me (**L1**)	12%
	R = Et (**L2**)	22%
	R = *i*-Pr (**L3**)	52%
	R = c-Pent (**L4**)	>99%

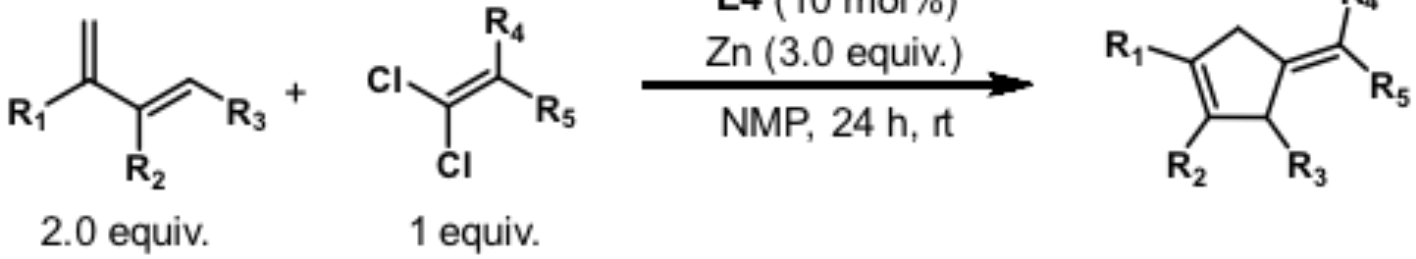
Mononucleating Ligands: no cycloaddition

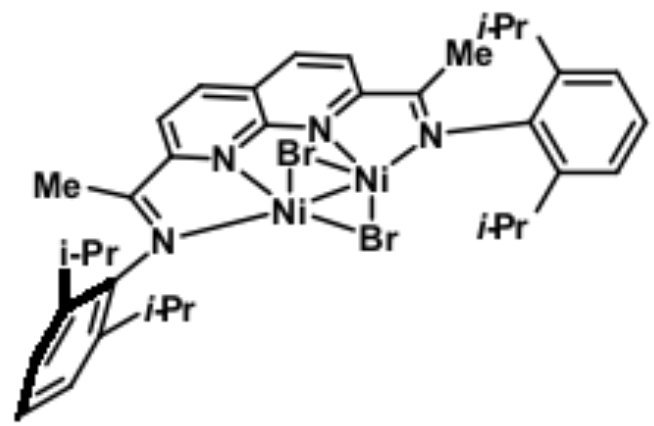


Uyeda, C., *Science*, **2019**, *363*, 857-862.

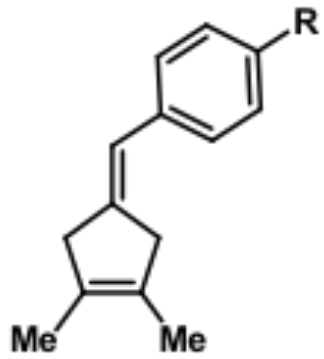
双核镍催化的烯基卡宾的[4+1]环加成反应

◆ 底物：

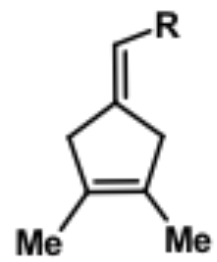




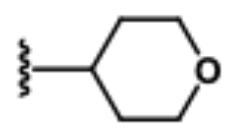
Selected Dichloroalkene Scope:



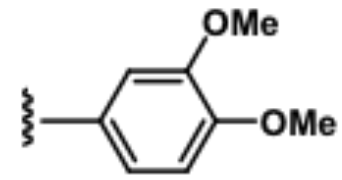
R = H	91% Yield
R = SMe	99% Yield
R = CF_3	73% Yield
R = Br	84% Yield
R = CN	84% Yield
R = CO_2Me	84% Yield
R = BPin	84% Yield



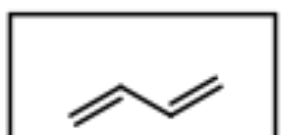
R =



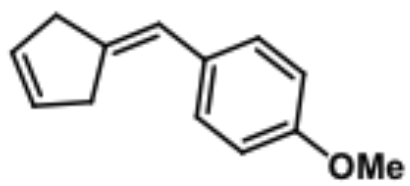
92% Yield



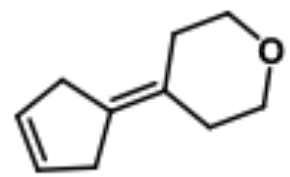
86% Yield



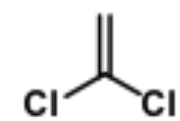
Butadiene



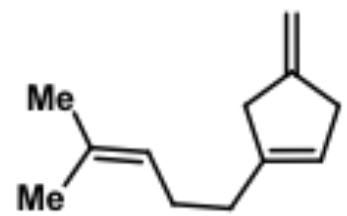
90% Yield



43% Yield



Parent Vinylidene

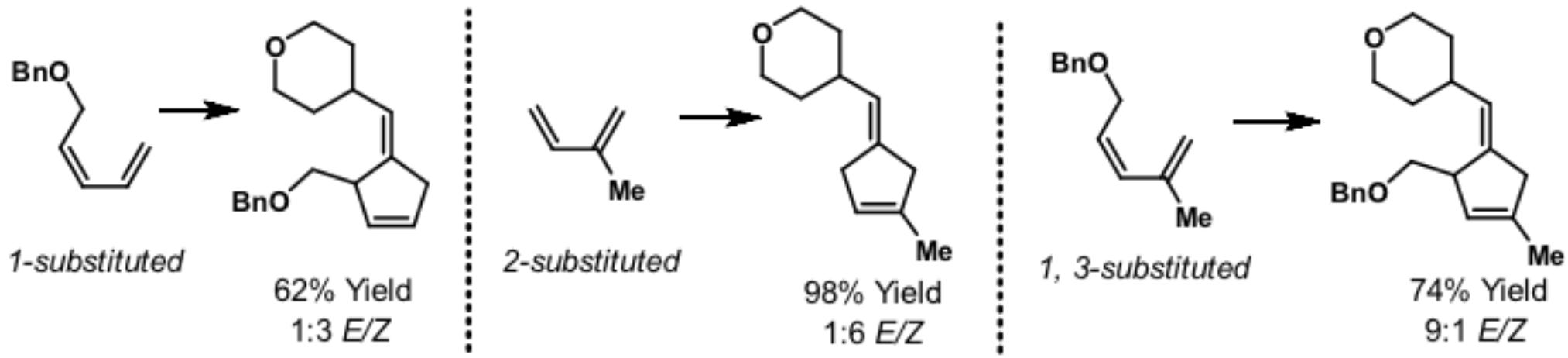


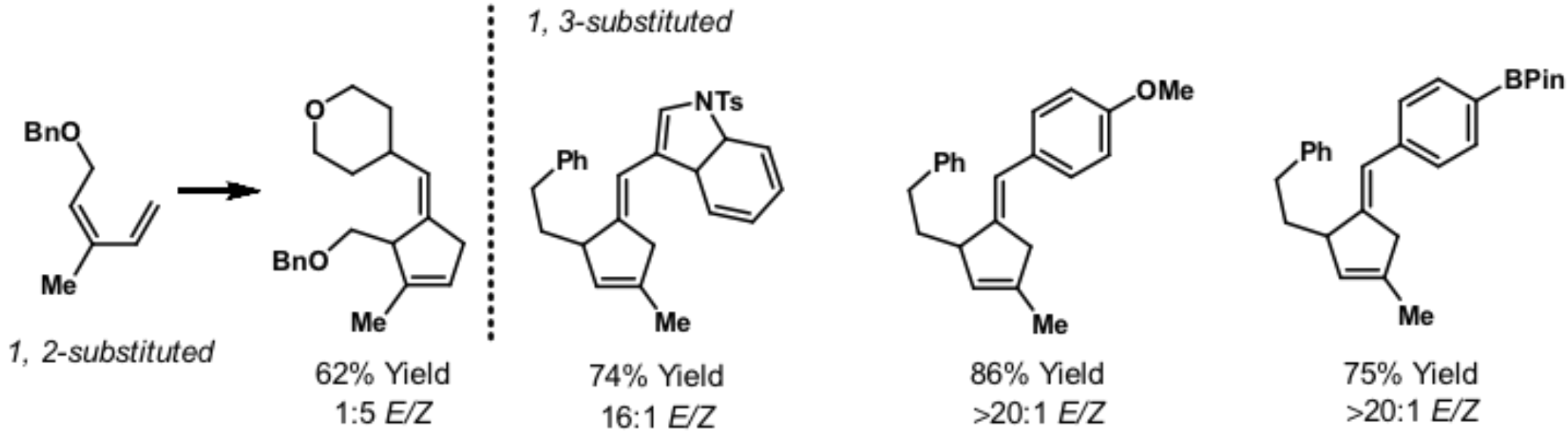
59% Yield

Uyeda, C., *Science*, **2019**, *363*, 857-862.

双核镍催化的烯基卡宾的[4+1]环加成反应

◆ 底物：

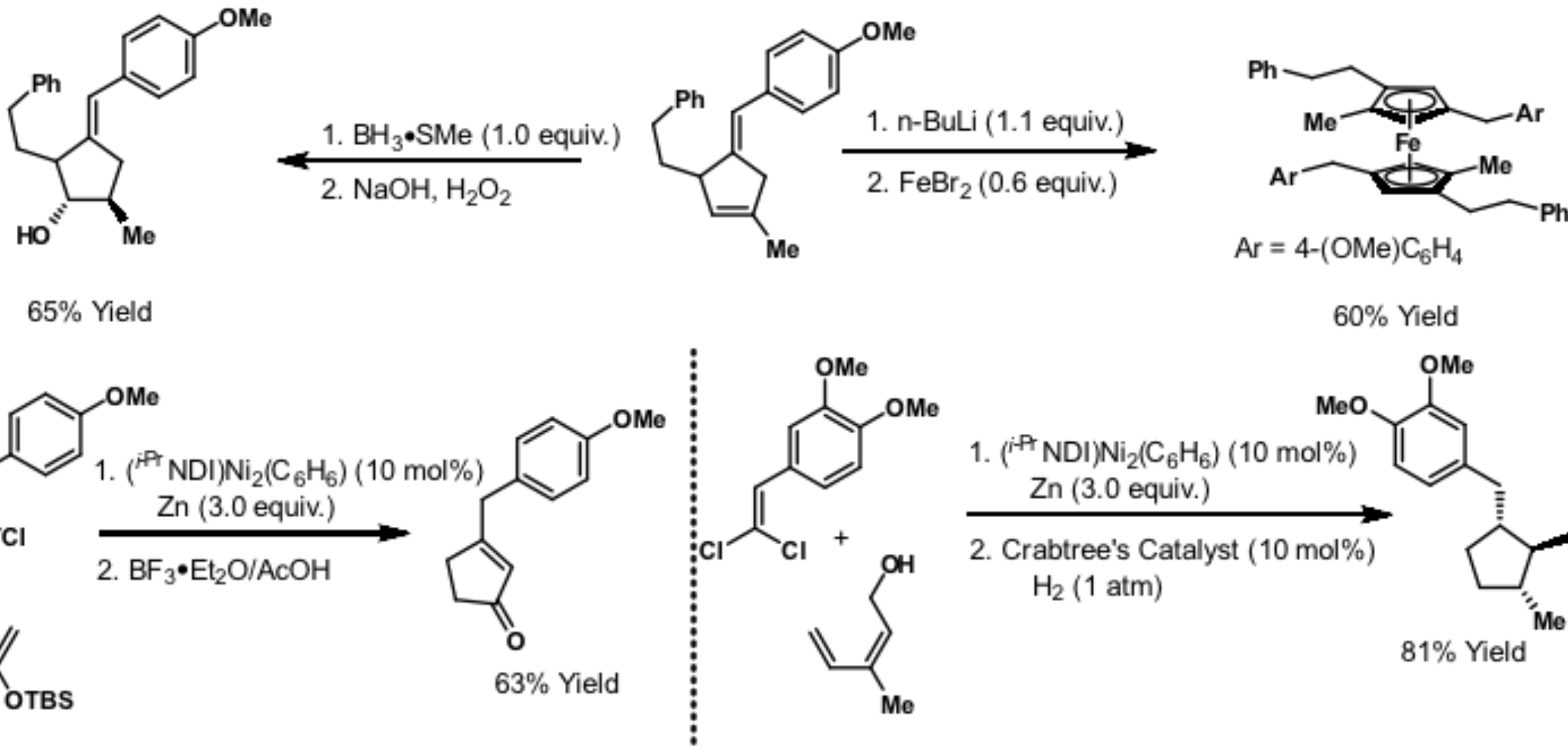




Uyeda, C., *Science*, **2019**, *363*, 857-862.

双核镍催化的烯基卡宾的[4+1]环加成反应

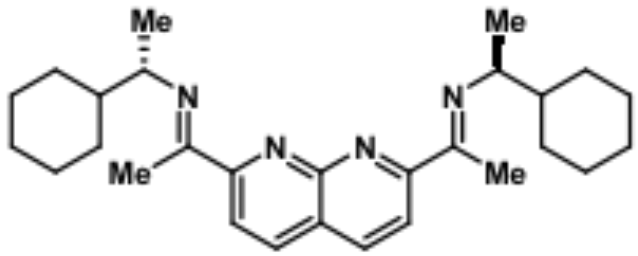
◆ 衍生化实验：



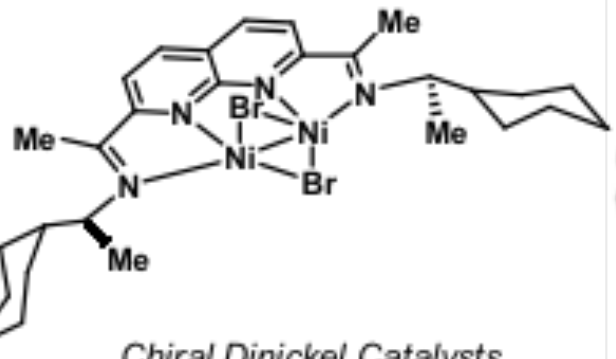
Uyeda, C., *Science*, **2019**, *363*, 857-862.

双核镍催化的烯基卡宾的[4+1]环加成反应

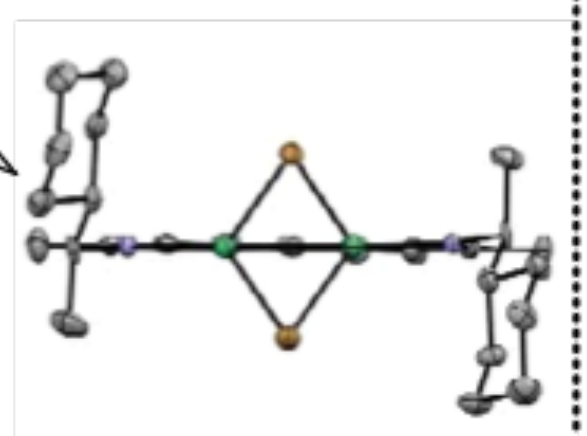
◆ 手性双核镍催化剂催化分子内的[4+1]反应

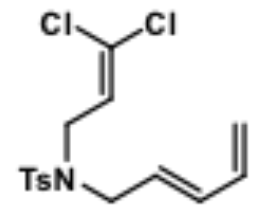


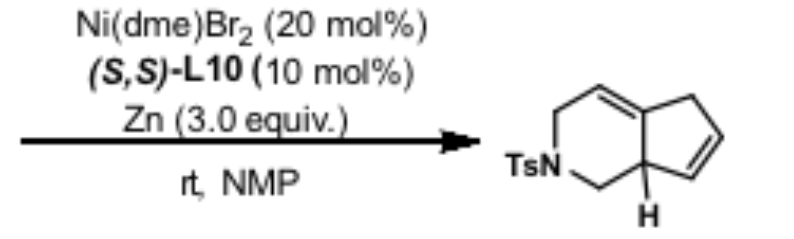
(S,S)-L10



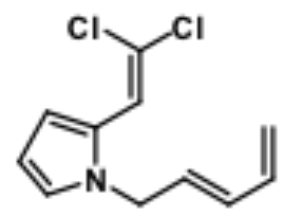
Chiral Dinickel Catalysts

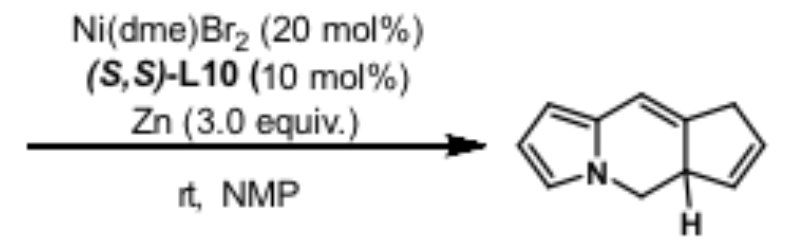




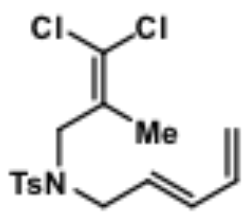


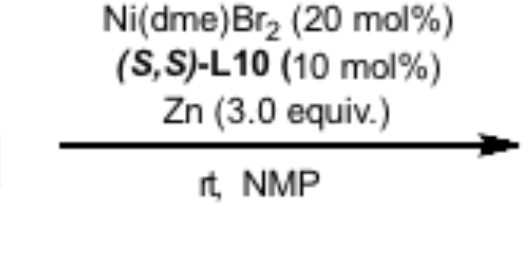
65% Yield, (90% *ee*)



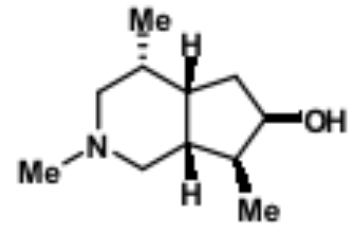


92% Yield, (86% *ee*)

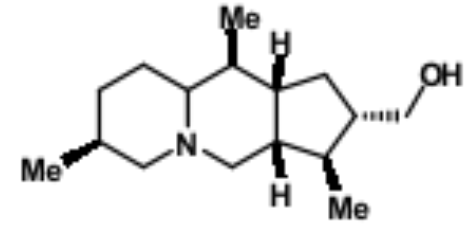




91% Yield
78% *ee*



Incarvilline



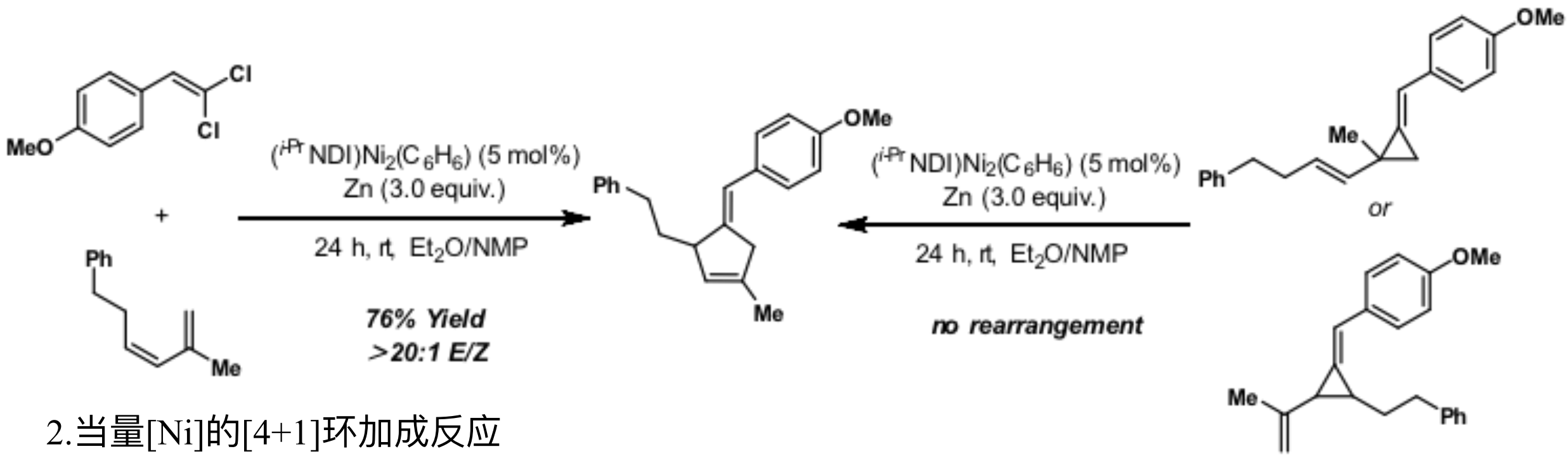
Alkaloid 251F

Uyeda, C., *Science*, **2019**, *363*, 857-862.

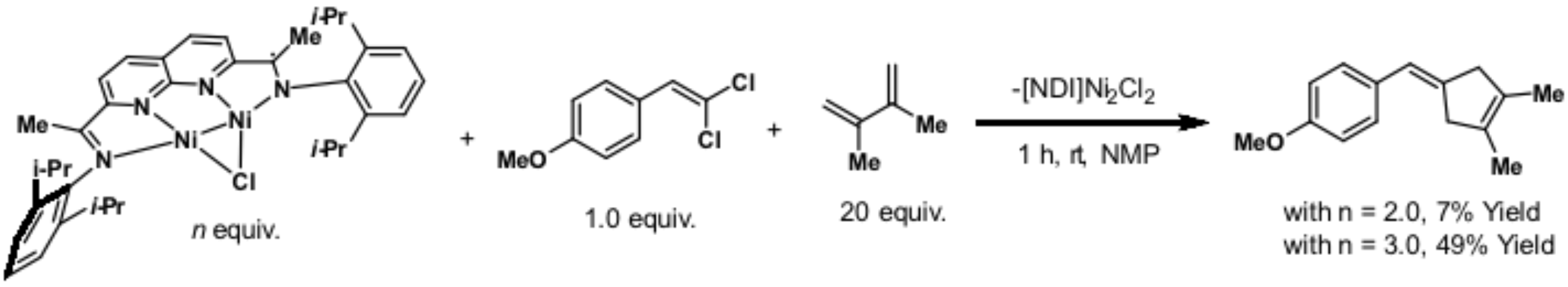
双核镍催化的烯基卡宾的[4+1]环加成反应

◆ 机理实验：

1.证明反应机理经历直接的[4+1]环加成还是[2+1]环加成/1,3-重排



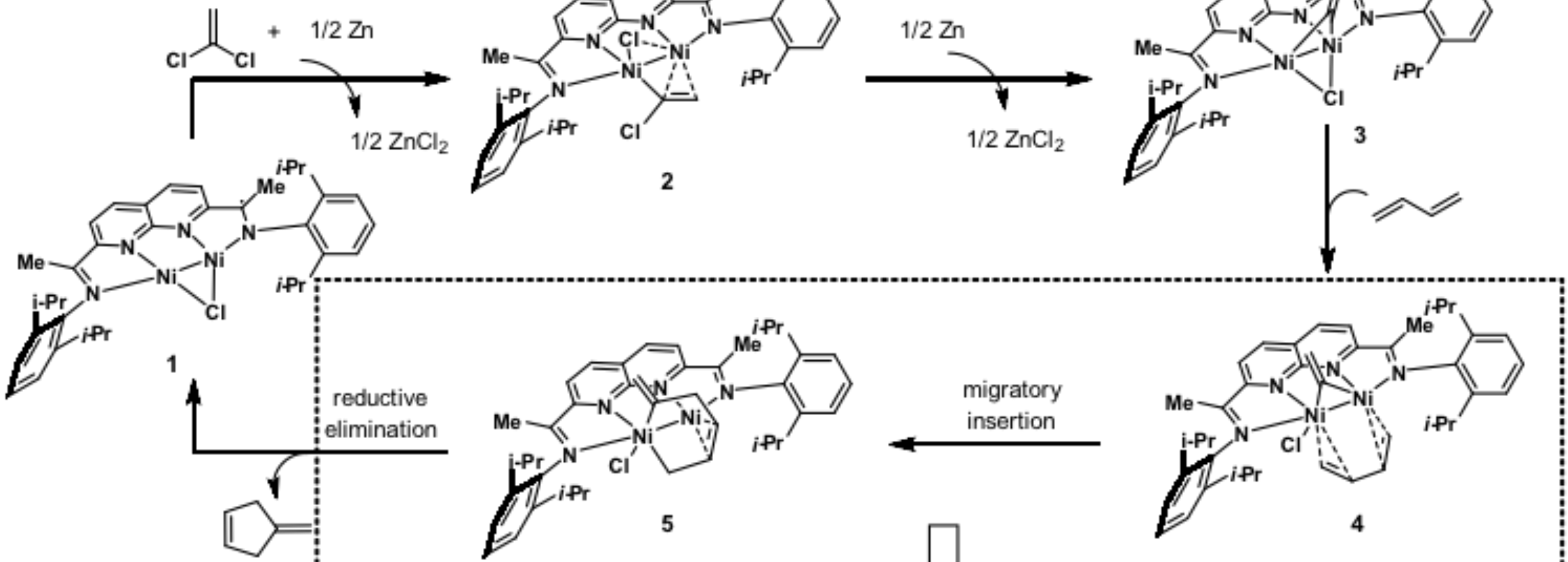
2.当量[Ni]的[4+1]环加成反应

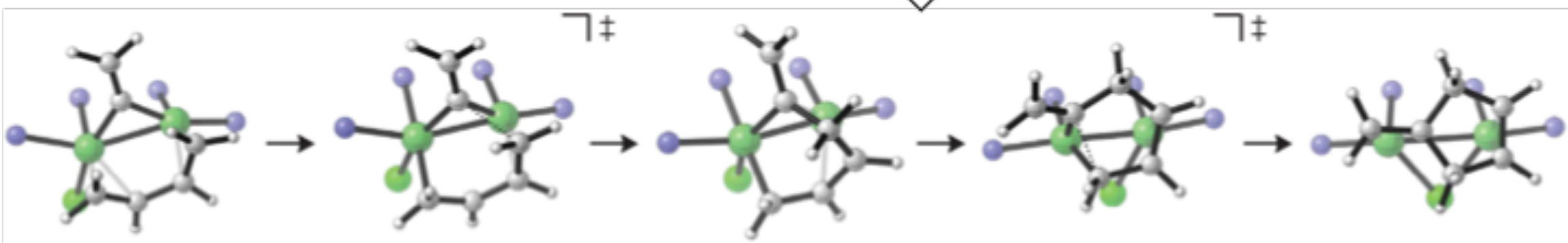


Uyeda, C., *Science*, **2019**, *363*, 857-862.

双核镍催化的烯基卡宾的[4+1]环加成反应

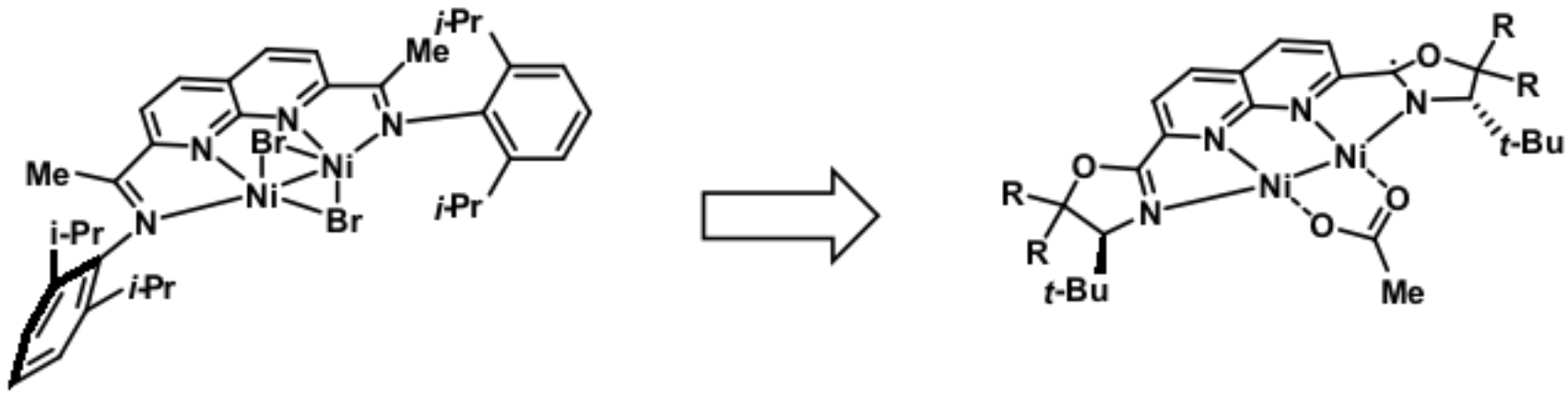
◆ 反应机理：





Uyeda, C., *Science*, **2019**, *363*, 857-862.

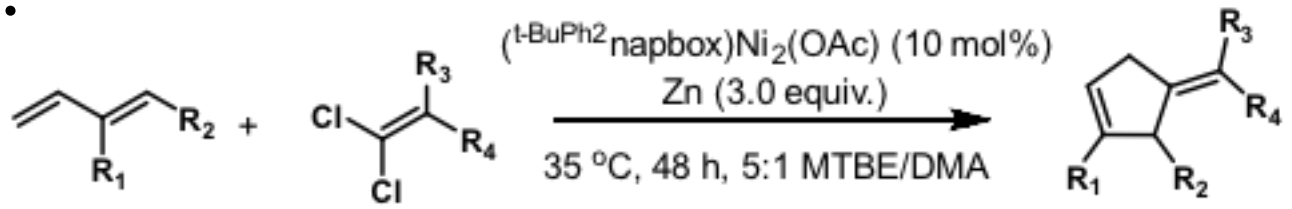
手性双核镍催化的烯基卡宾的[4+1]环加成反应



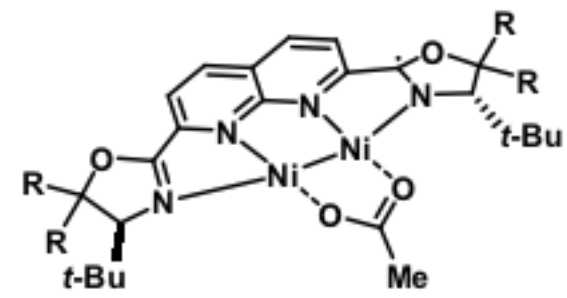
Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 17294-17300

手性双核镍催化的烯基卡宾的[4+1]环加成反应

◆ 底物：

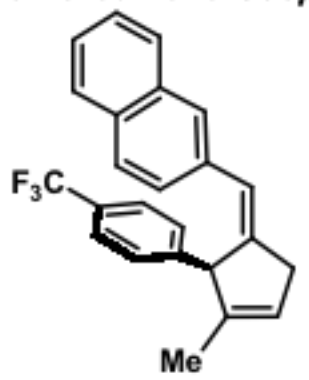


2.0 equiv. 1.0 equiv.

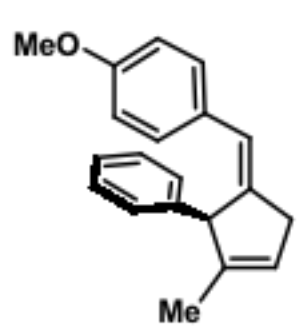


R = Ph ($^{t\text{-BuPh2}}$napbox)Ni_2(OAc)

1,1-dichloroalkene Scope

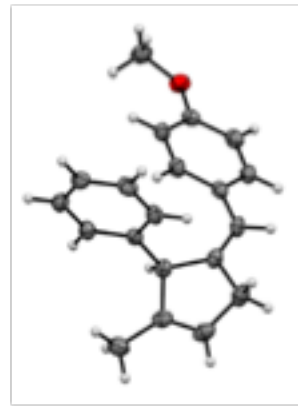


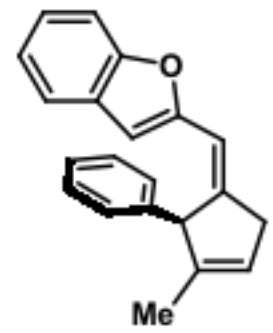
75% Yield
98% *ee*, >20:1 *Z/E*



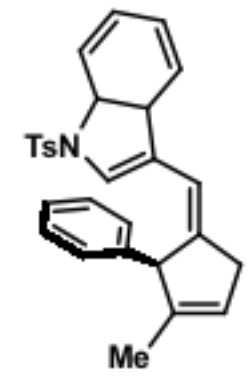
78% Yield
96% *ee*, >20:1 *Z/E*

=



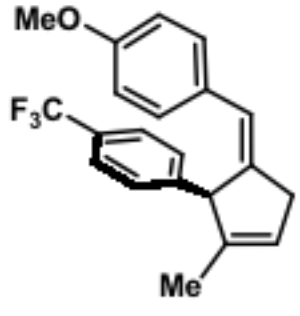


53% Yield
89% *ee*, 6:1 *Z/E*

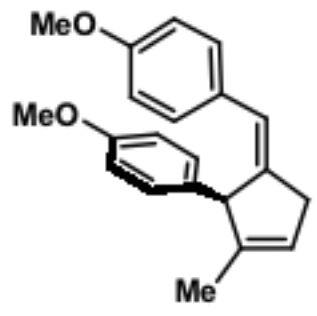


70% Yield
91% *ee*, 14:1 *Z/E*

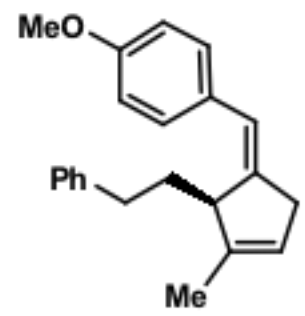
1,3-diene Scope



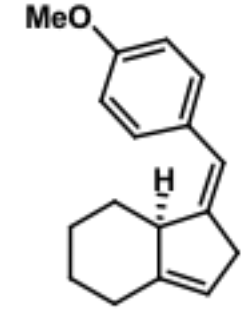
83% Yield
98% *ee*, >20:1 *Z/E*



73% Yield
98% *ee*, >20:1 *Z/E*



59% Yield
83% *ee*, 9:1 *Z/E*

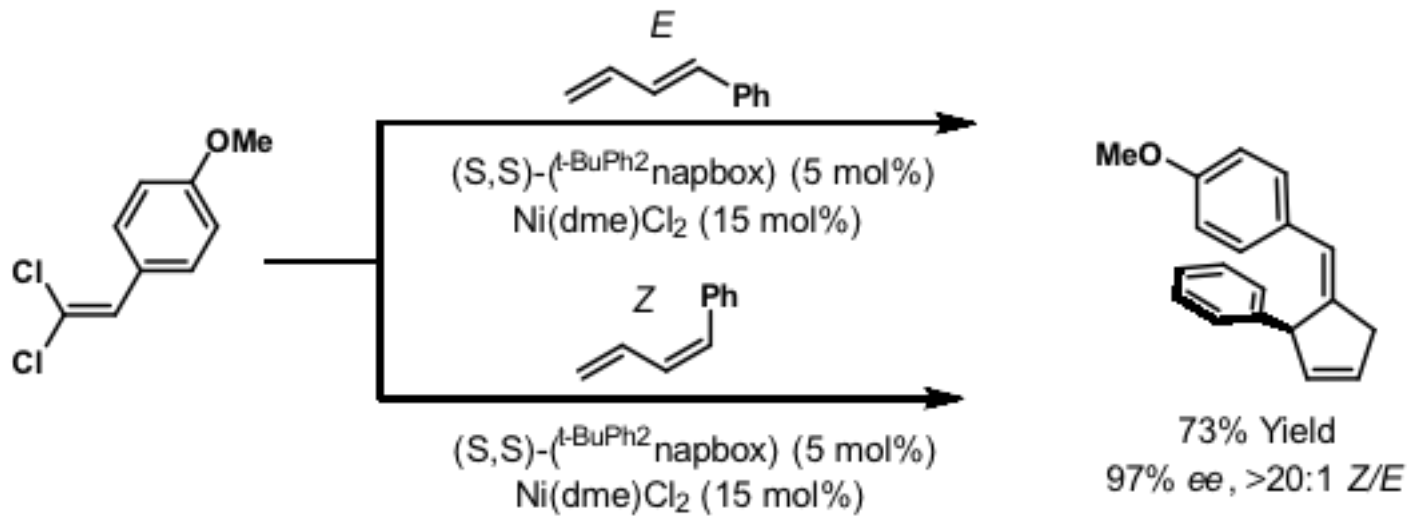


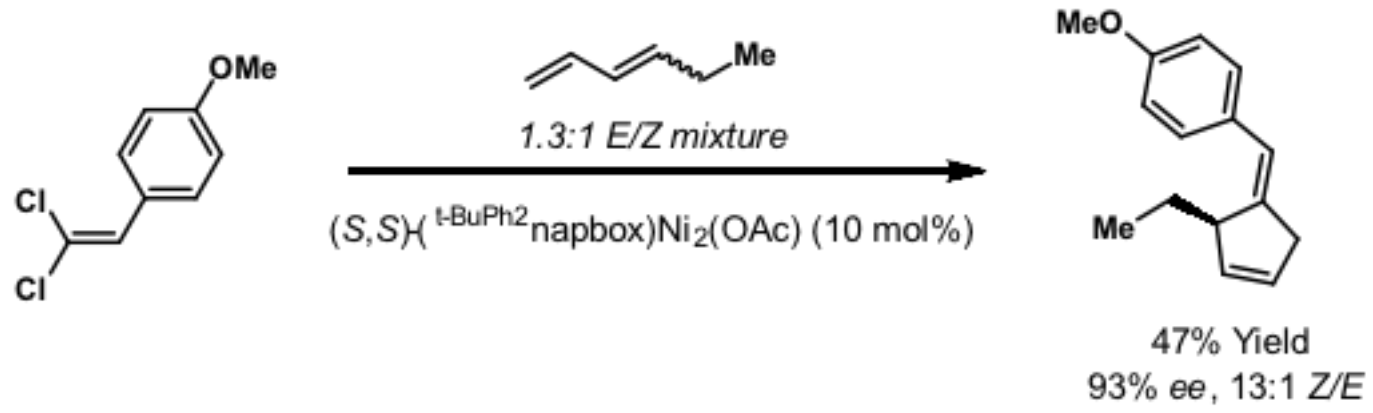
43% Yield
74% *ee*, >20:1 *Z/E*

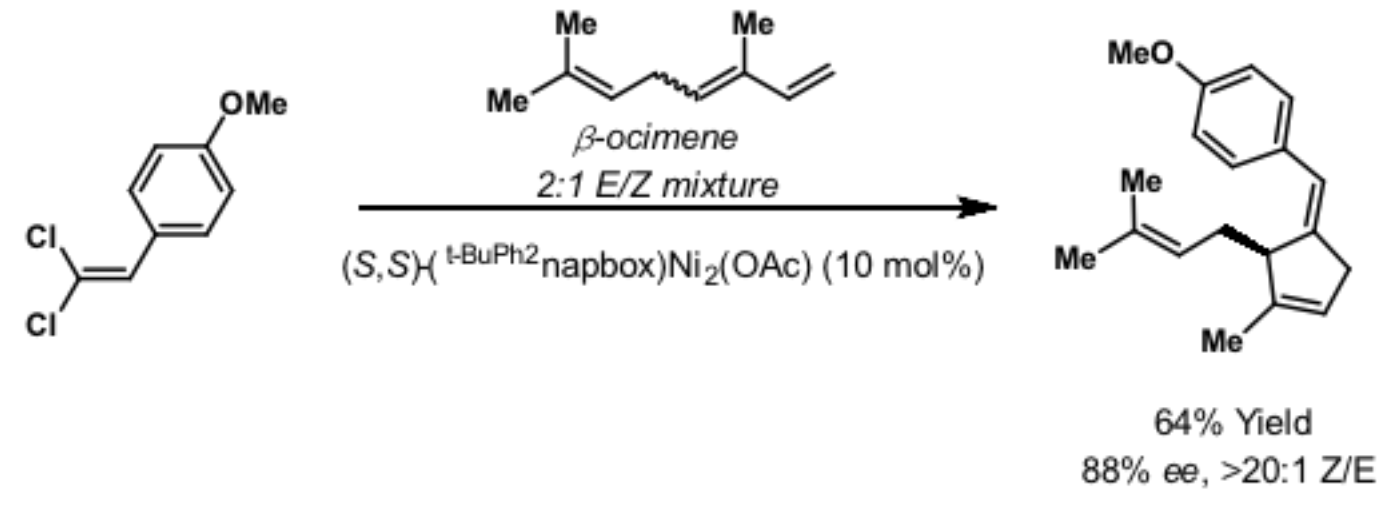
Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 17294-17300

手性双核镍催化的烯基卡宾的[4+1]环加成反应

◆ 构型实验：



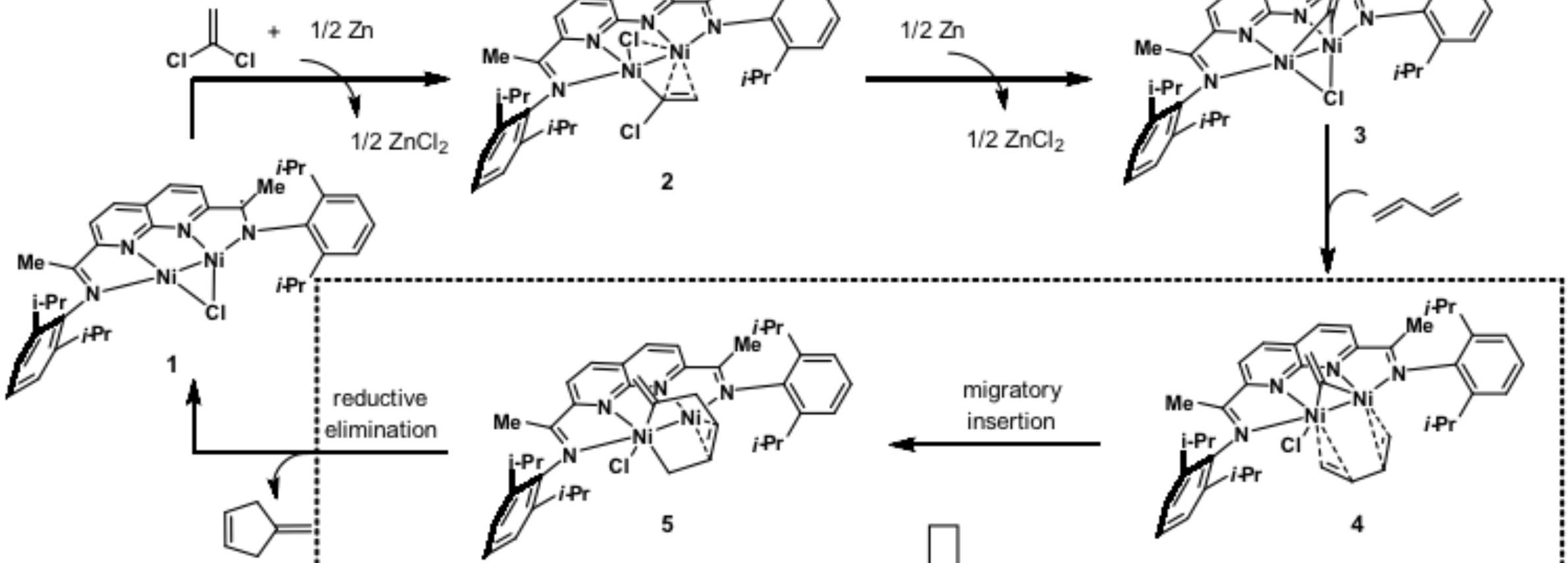


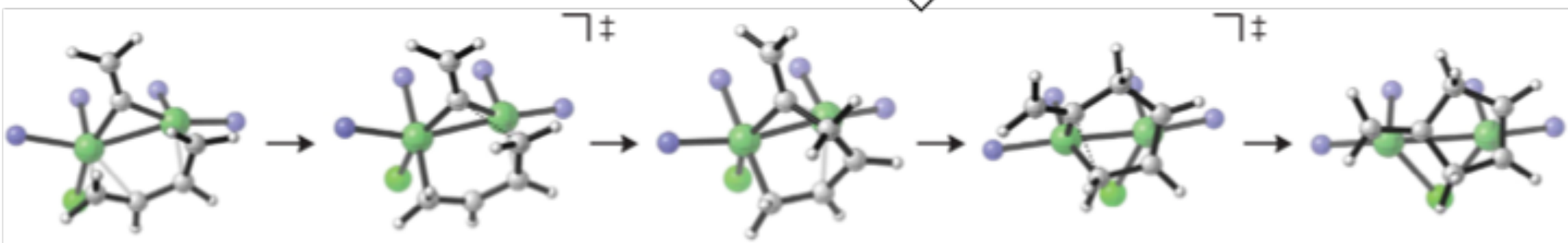


Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 17294-17300

双核镍催化的烯基卡宾的[4+1]环加成反应

◆ 反应机理：

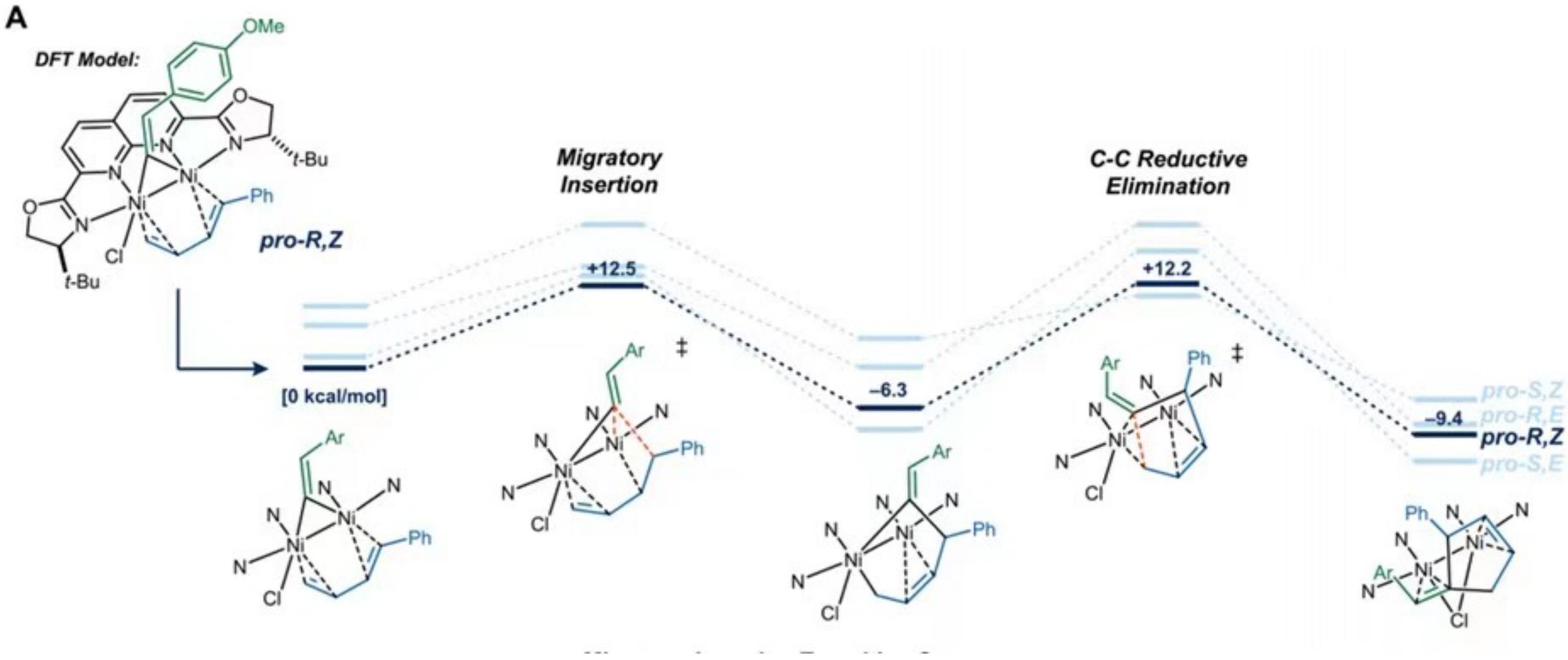




Uyeda, C., *Science*, **2019**, *363*, 857-862.

手性双核镍催化的烯基卡宾的[4+1]环加成反应

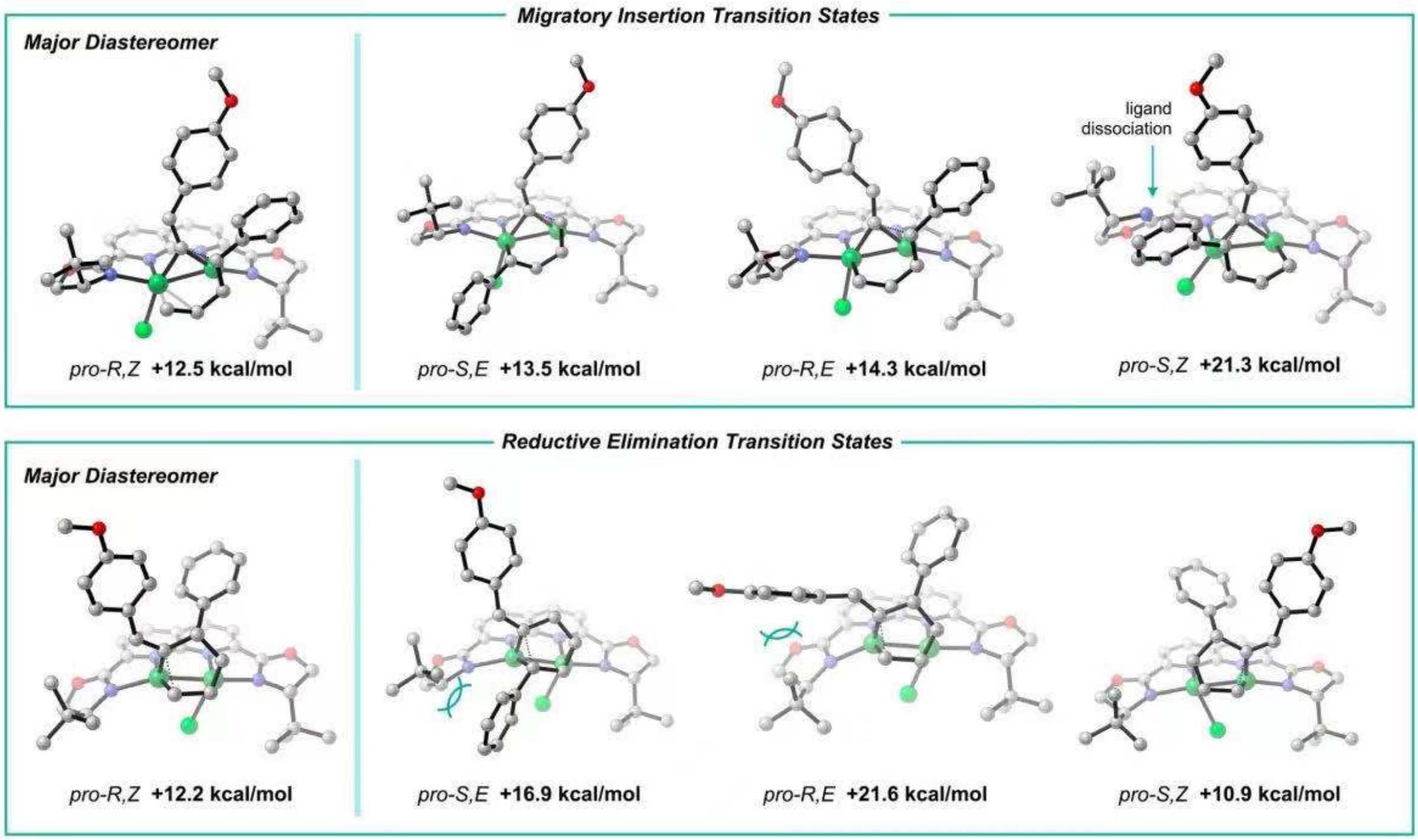
◆ **DFT计算：**



Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 17294-17300

手性双核镍催化的烯基卡宾的[4+1]环加成反应

B



Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 17294-17300

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2. 双核镍催化剂简介

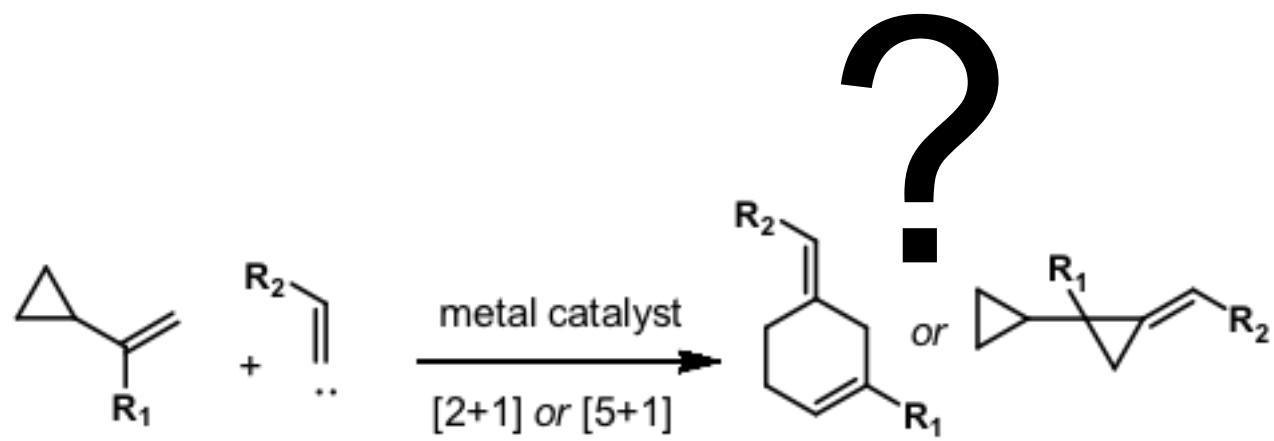
3. 双核镍催化的烯基卡宾的环加成反应

4. 钴催化的卡宾的环加成反应

5. 总结

钴催化的烯基卡宾的[5+1]环加成反应

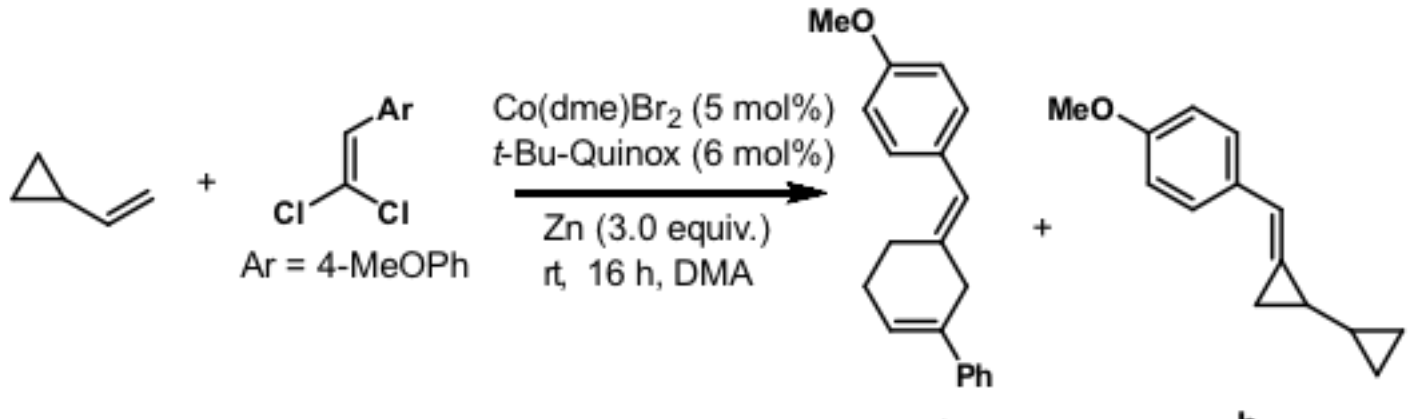
环丙烷乙烯发生[5+1]的挑战

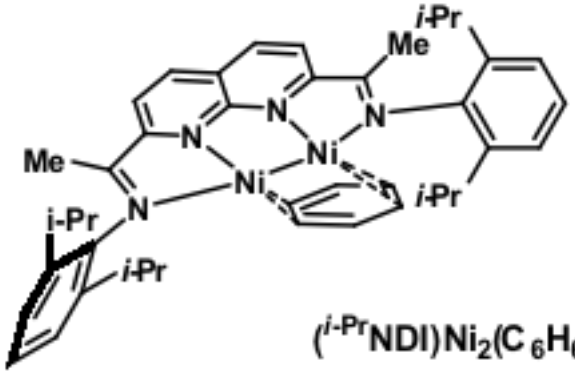


Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 4598−4603

钴催化的烯基卡宾的[5+1]环加成反应

双核镍催化剂与钴催化剂的对比：





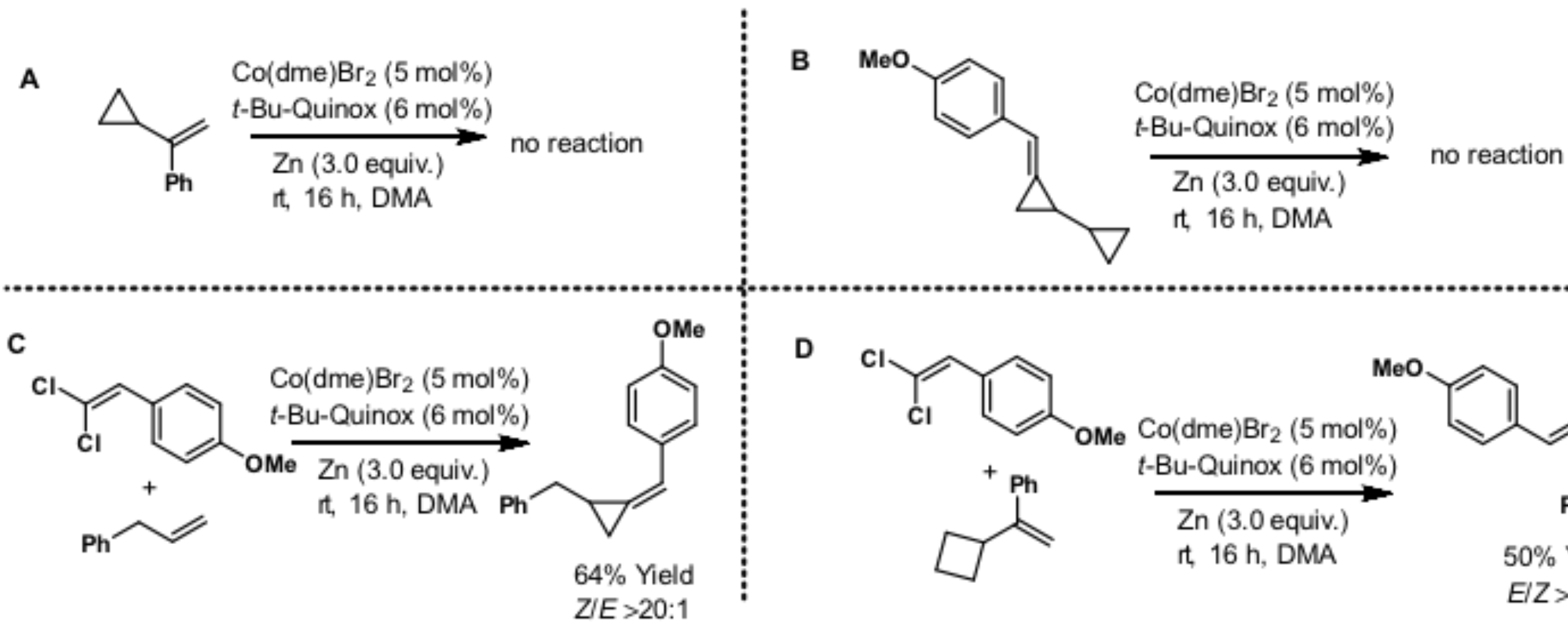
($^{i\text{-Pr}}$NDI)$Ni_2(C_6H_6)$

($^{t\text{-Bu}}$Quinox)Co

Combined Yield (**a+b**)	87%	90%
[5+1] vs. [2+1] (**a:b**)	1:1	>20:1
Setreoselectivity (**b-*E*:b-*Z***)	1:3	>20:1

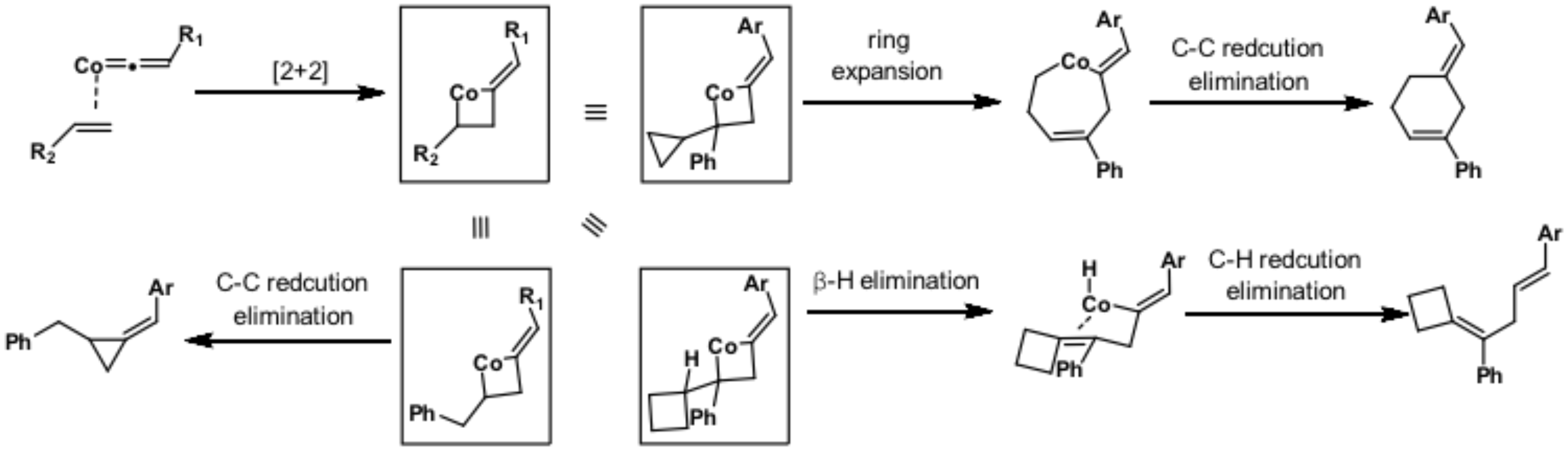
Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 4598−4603

◆ **控制实验：**



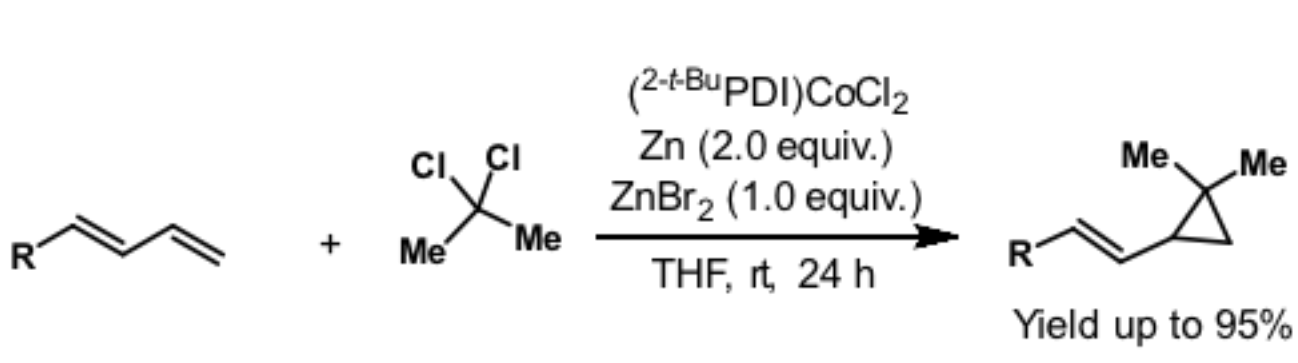
Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 4598−4603

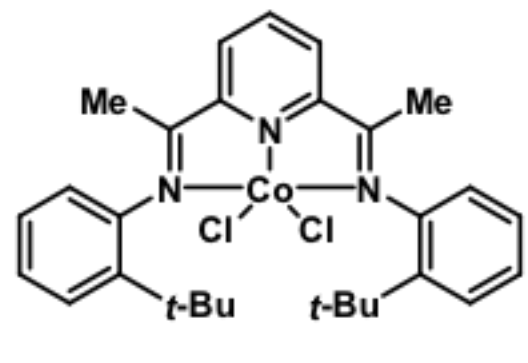
◆ 反应机理：

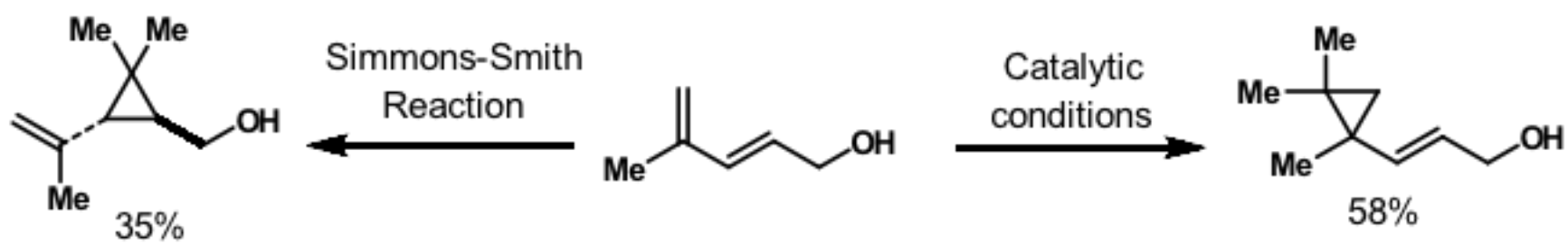


Uyeda, C *J. Am. Chem. Soc.* **2020**, *142*, 4598−4603

钴催化的卡宾的[2+1]环加成反应

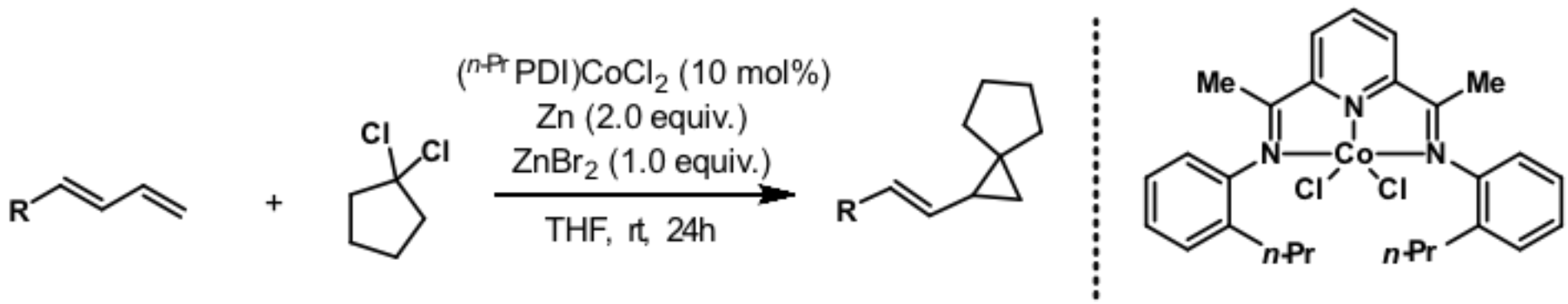


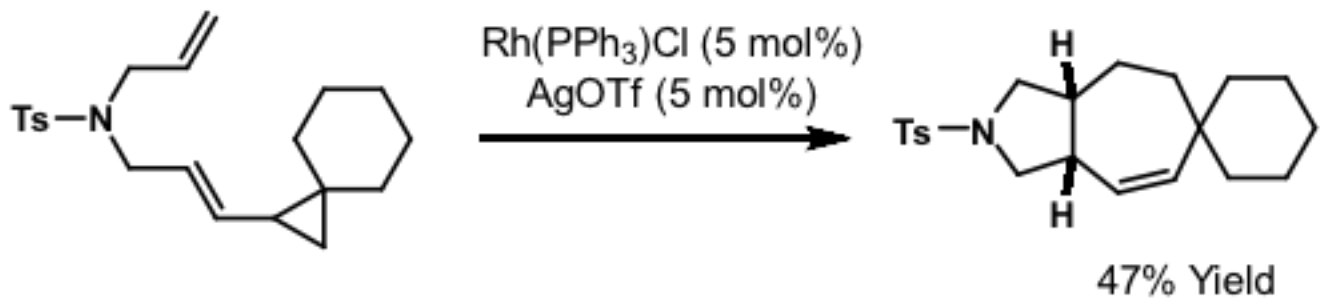




Uyeda, *C , Angew. Chem. Int. Ed*. **2018**, *57*, 13902 –13906

钴催化的卡宾的[2+1]环加成反应

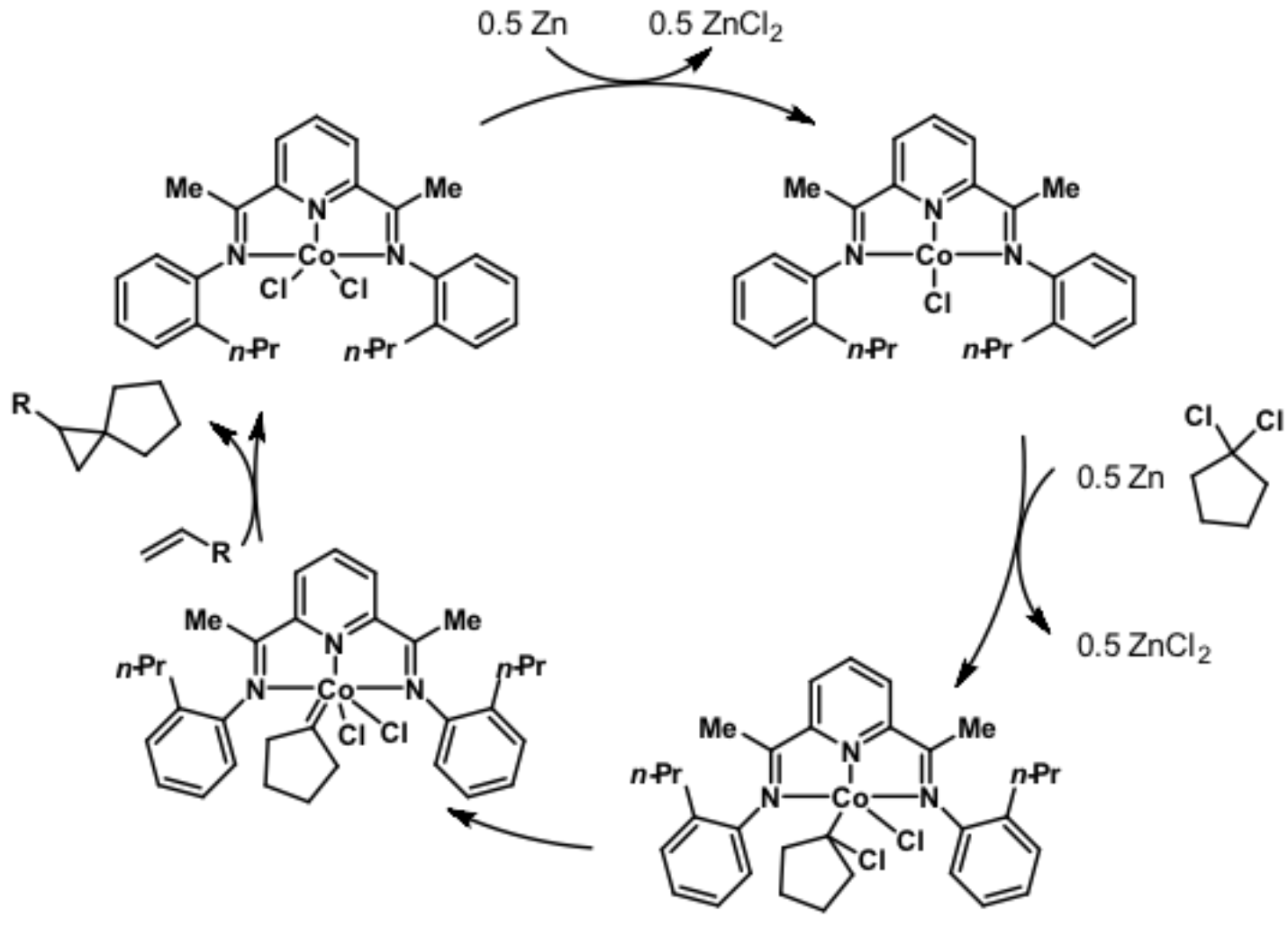




Uyeda, *C Adv. Synth. Catal*. **2020**, *362*, 348 -352

钴催化的卡宾的[2+1]环加成反应

◆ 反应机理：



Uyeda, *C Adv. Synth. Catal*. **2020**, *362*, 348 -352

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1.3 烯基卡宾参与的反应

2. 双核镍催化剂简介

3. 双核镍催化的烯基卡宾的环加成反应

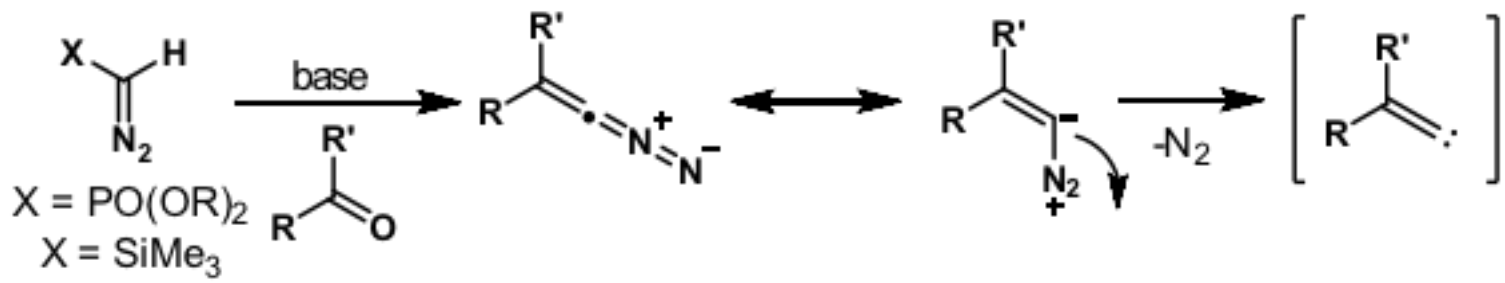
4. 钴催化的卡宾的环加成反应

5. 总结

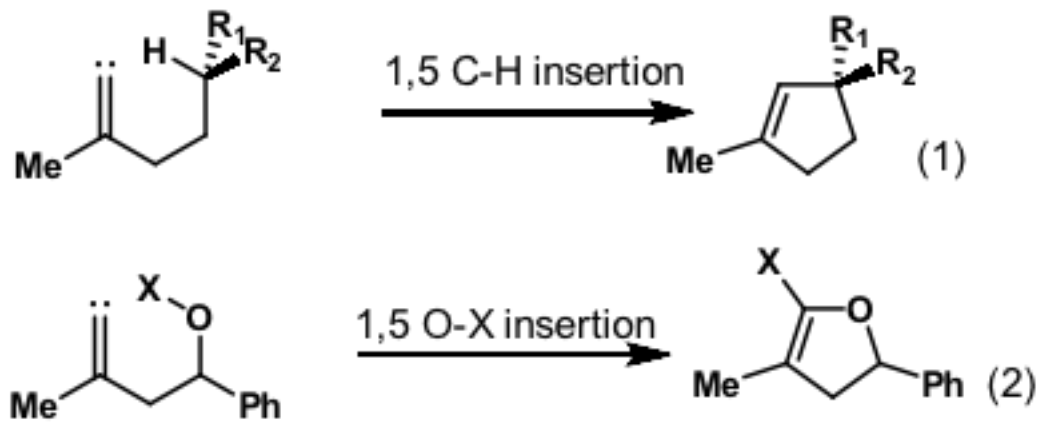
总结

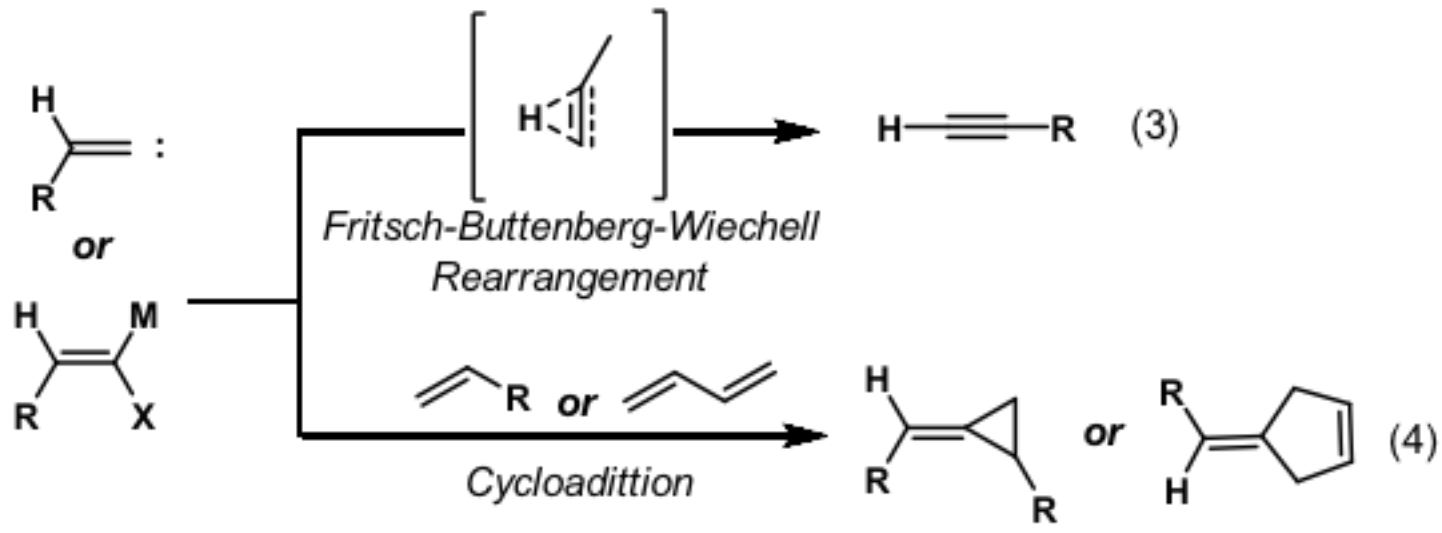
◆ 烯基卡宾的结构

◆ 烯基卡宾的生成方式

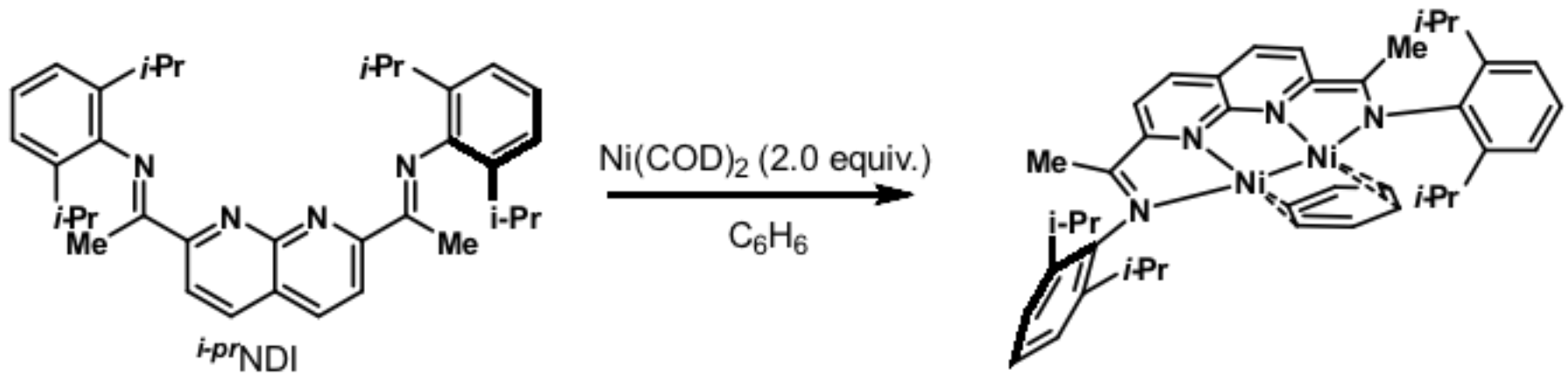


◆ 烯基卡宾参与的反应


1,5 C-H insertion
(1)
1,5 O-X insertion
(2)

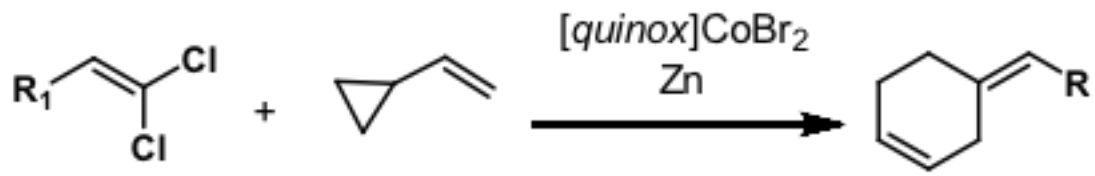

or
Fritsch-Buttenberg-Wiechell
Rearrangement
(3)
or
Cycloadittion
or
(4)

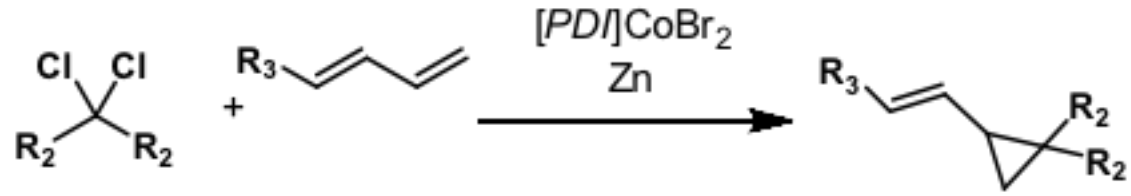
◆ 双核镍催化剂及其催化的[2+1]和[4+1]反应



总结

◆ 钴催化的[2+1]和[5+1]反应





请各位老师同学批评指正！

谢谢！