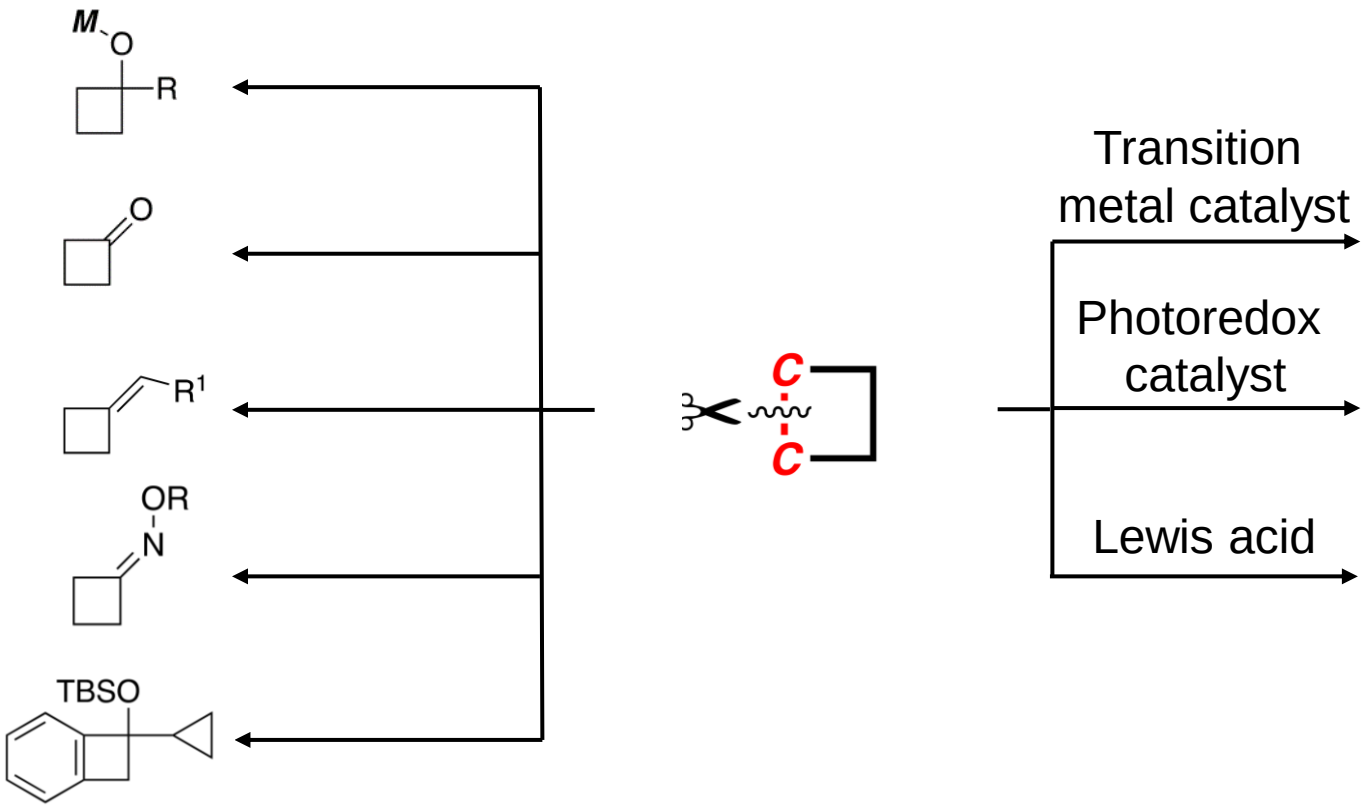
Cleavage of Carbon−Carbonσ-Bonds of Four-Membered Rings by Oxidative addition and Ring metallization

Xu Weiwei

2021-8-16

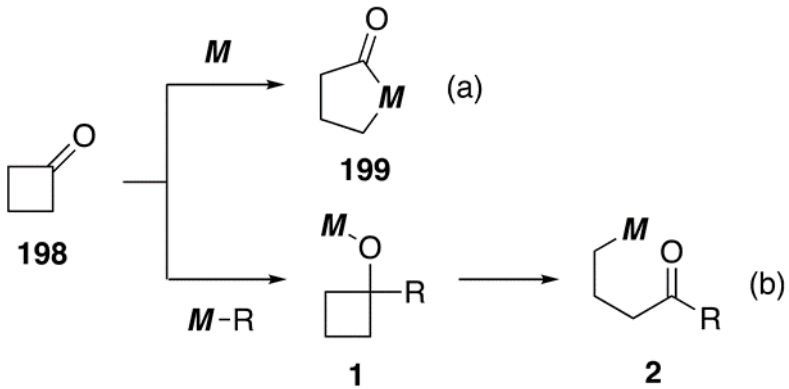
Rf: *Chem. Rev.* **2021**, *121*, 264−299

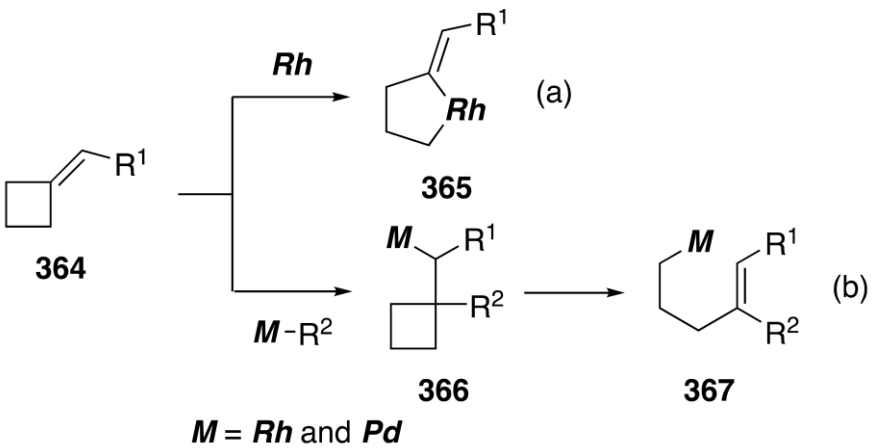
Literature report



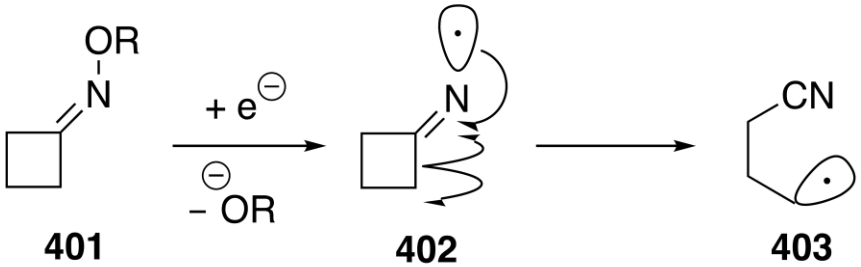
Literature report

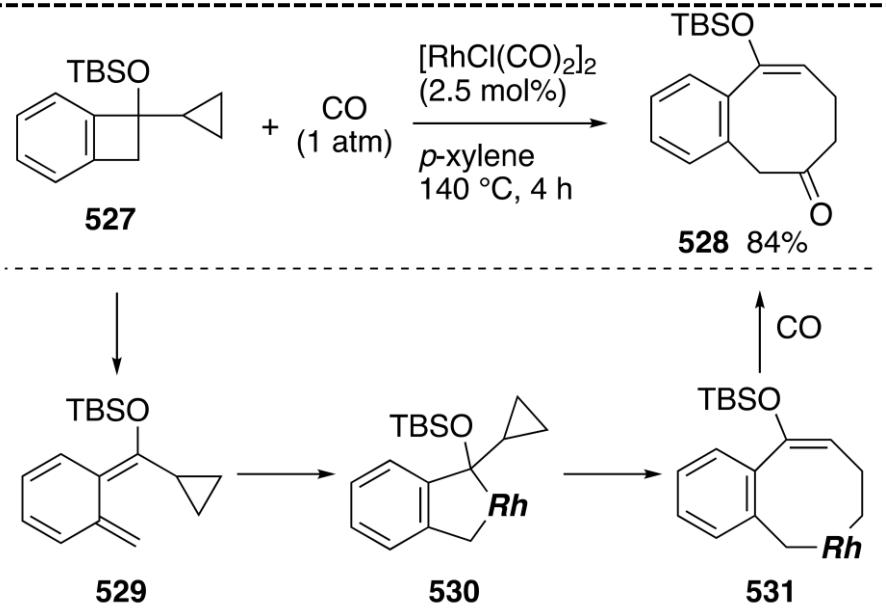
Transition metal catalyst





Others





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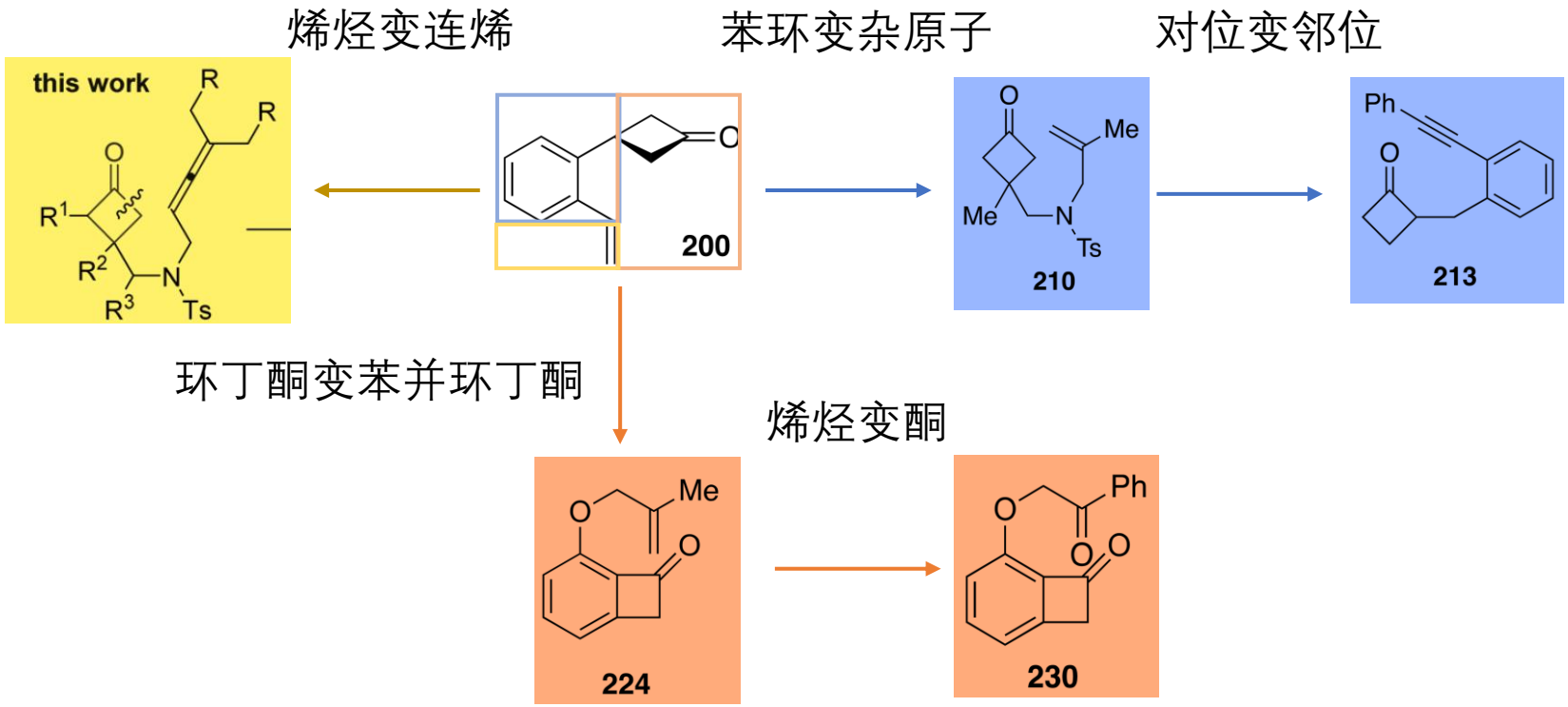
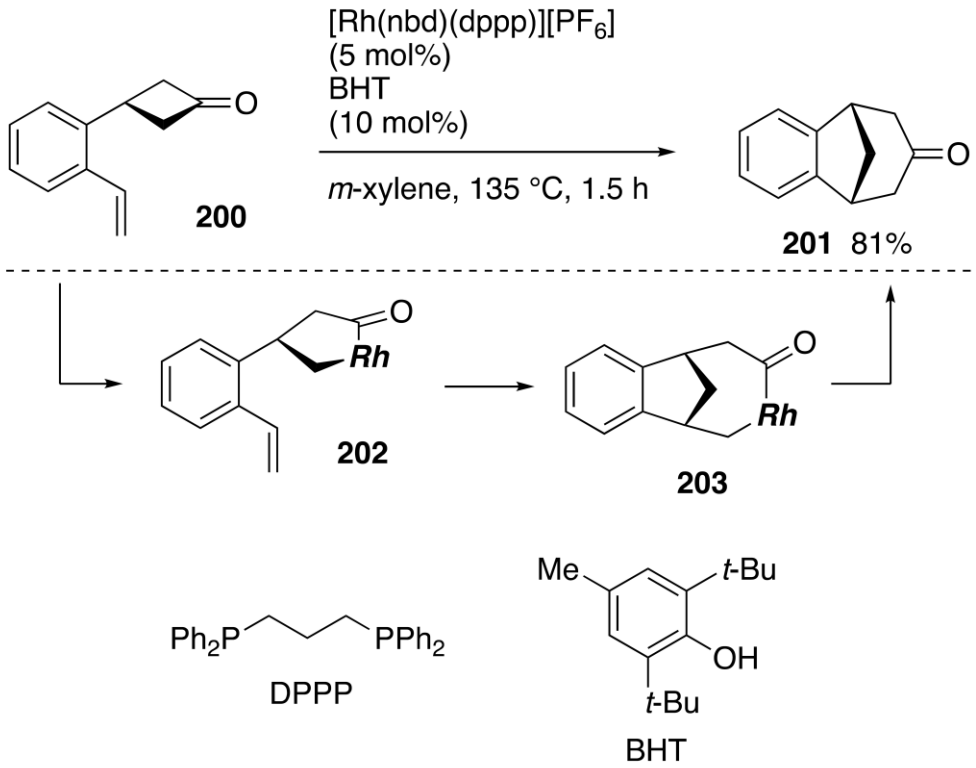
Rhodium Catalysis - process



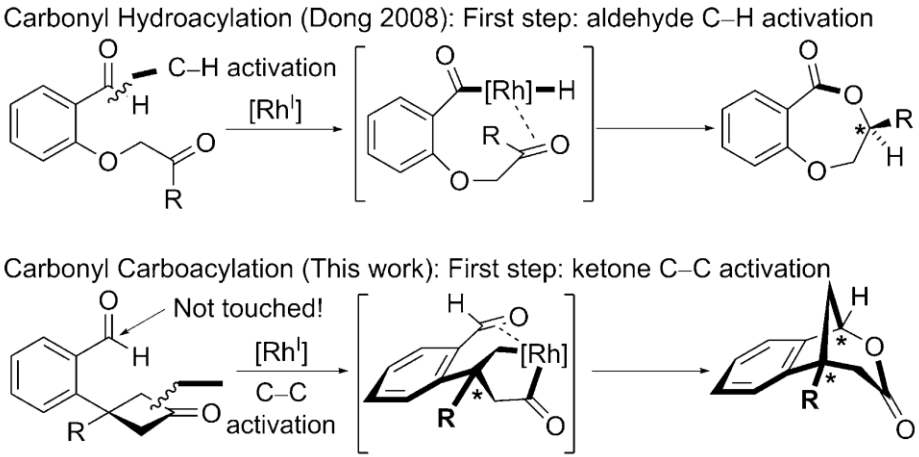
Rhodium Catalysis - Cyclobutanones

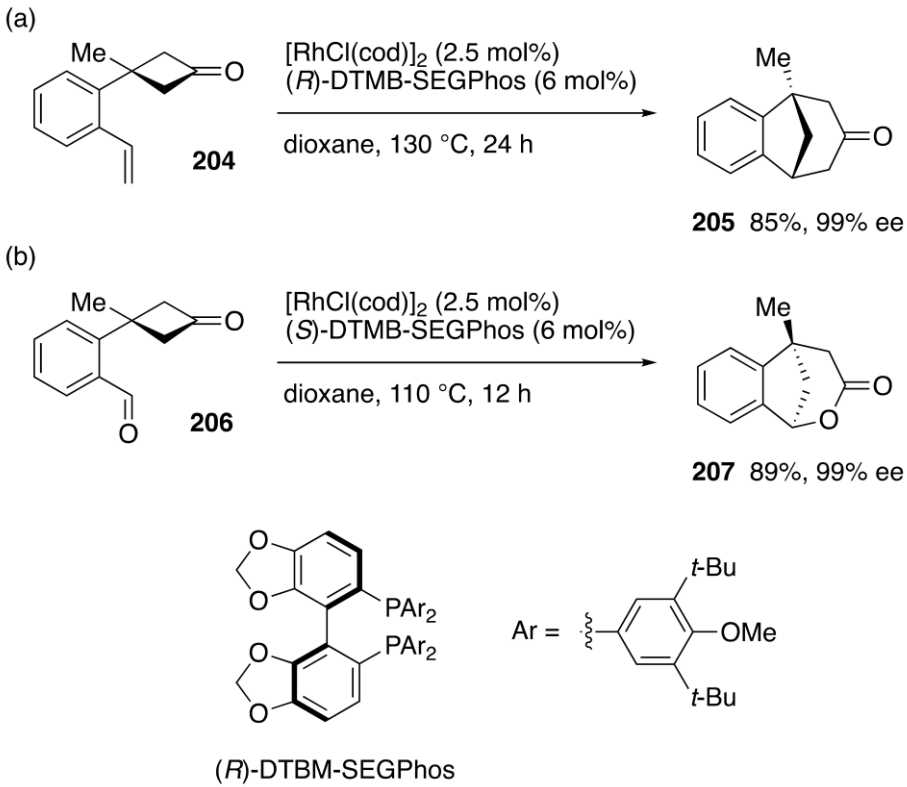


BHT的作用?

Murakami, M.; *J. Am. Chem. Soc*. **2002**, *124*, 13976−13977.

Rhodium Catalysis - Cyclobutanones

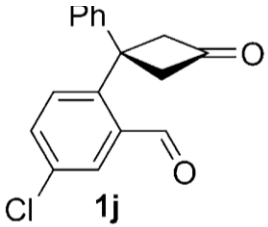


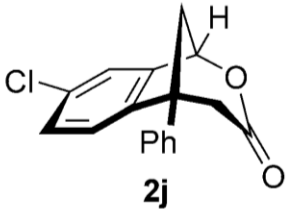


首例不对称

Cramer, N.; *Angew. Chem., Int. Ed.* **2014**, *53*, 3001−3005; Organometallics 2014, 33, 780−787.
Cramer, N.; *Angew. Chem., Int. Ed*. **2014**, *53*, 9640−9644.

Rhodium Catalysis - Cyclobutanones





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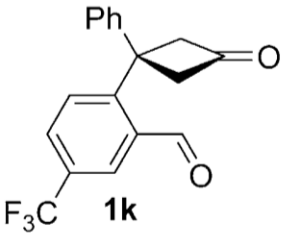

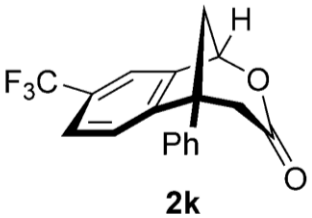

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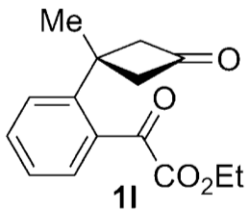

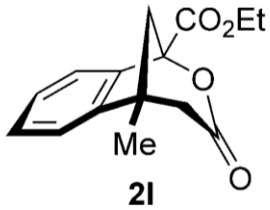

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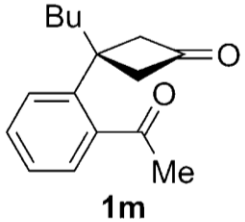
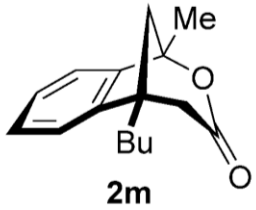
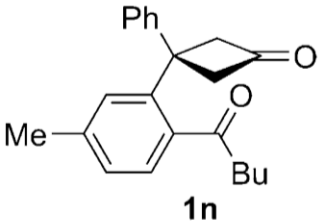
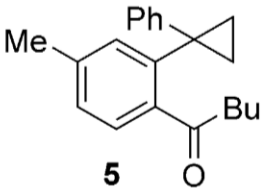




81 99.8:0.2





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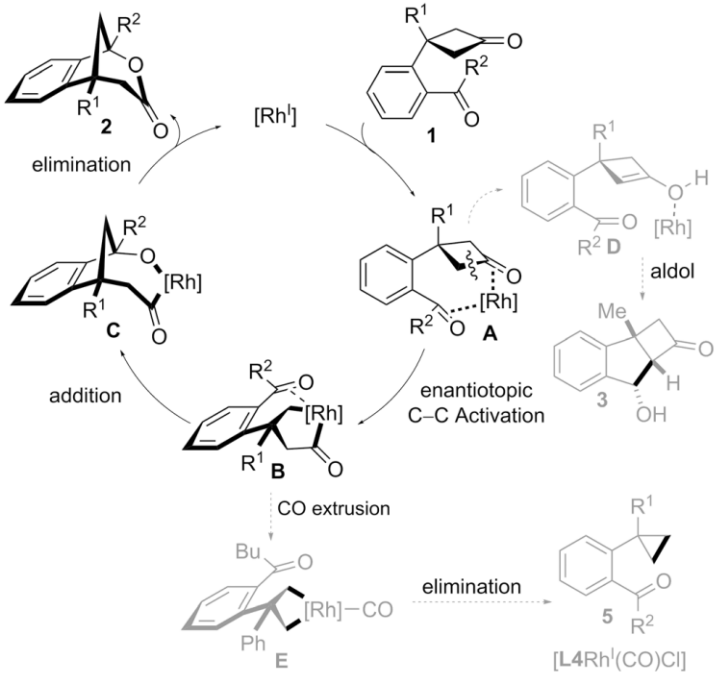
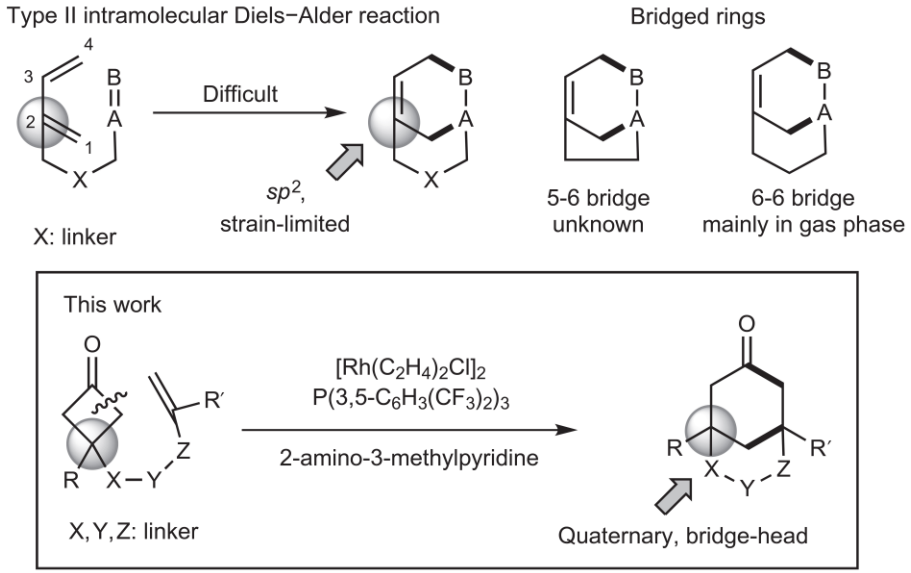
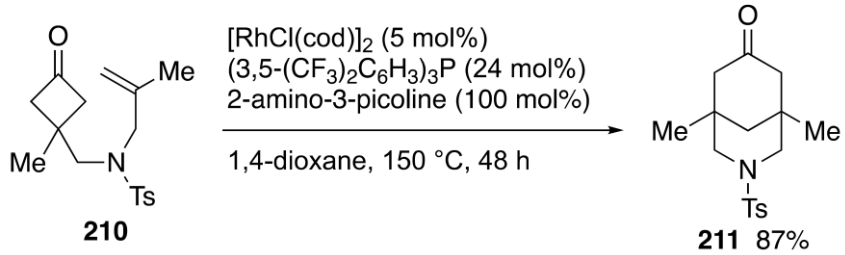


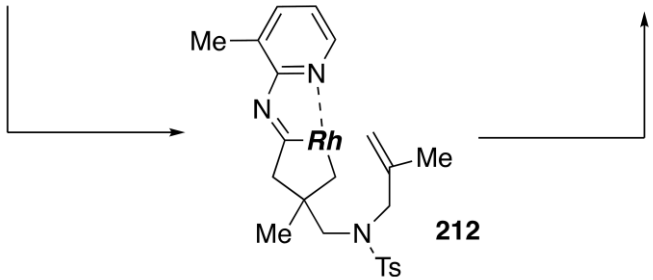
苯环必须存在

Rhodium Catalysis - Cyclobutanones





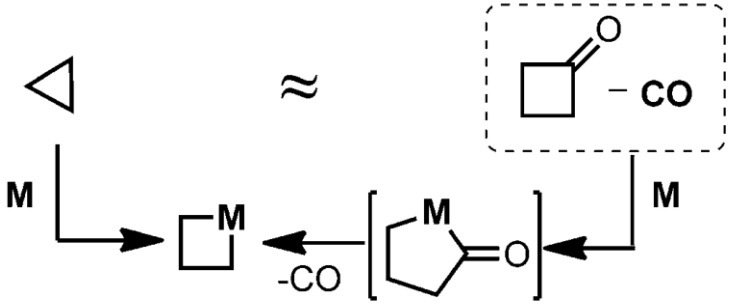
苯环拓成杂原子
杂原子必须

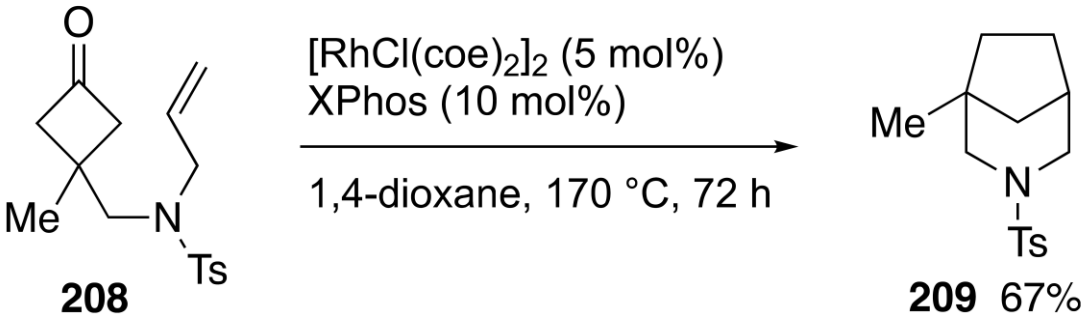


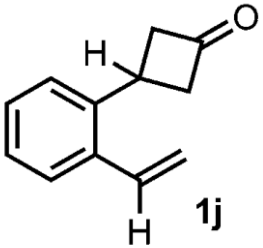
Dong, G.; *Nat. Chem.* **2014**, *6*, 739−744.

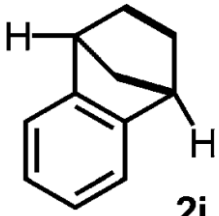
Rhodium Catalysis - Cyclobutanones

c) Cyclobutanone as a cyclopropane surrogate





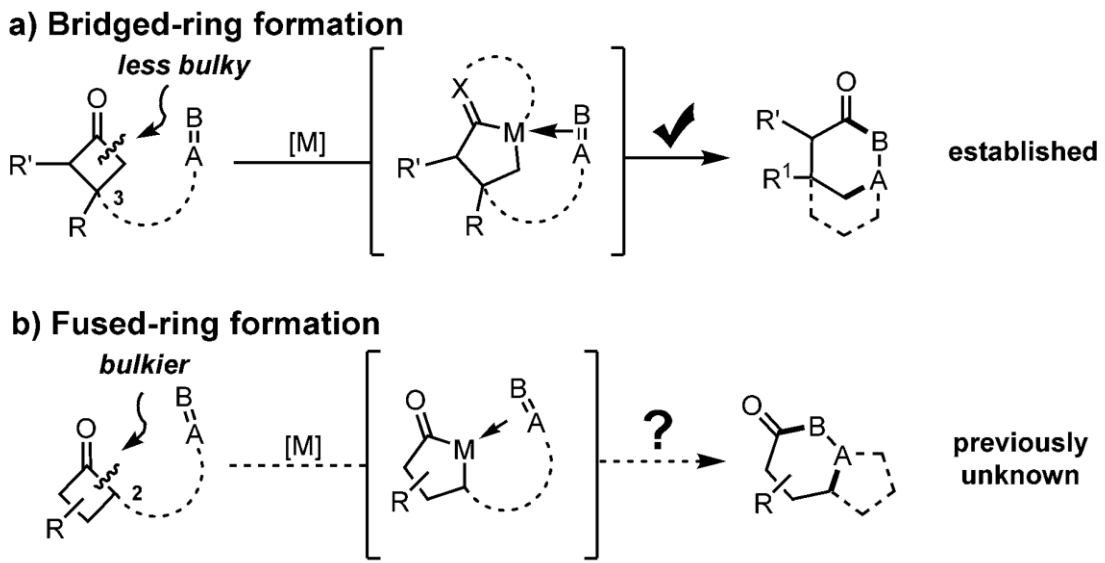


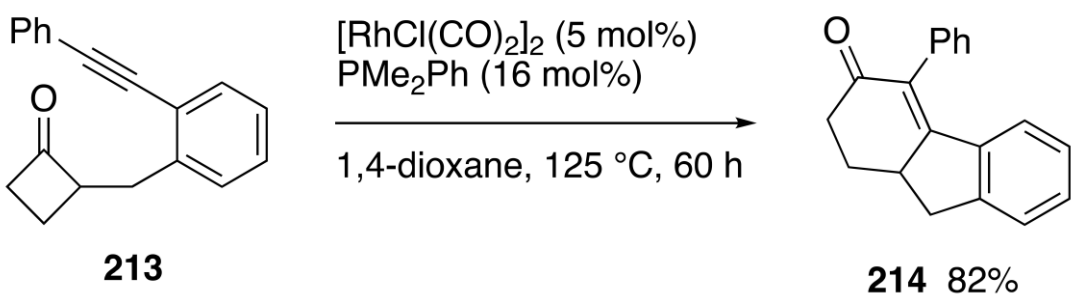


脱羰

Dong, G.; *Angew. Chem., Int. Ed*. **2016**, *55*, 13867−13871.

Rhodium Catalysis - Cyclobutanones

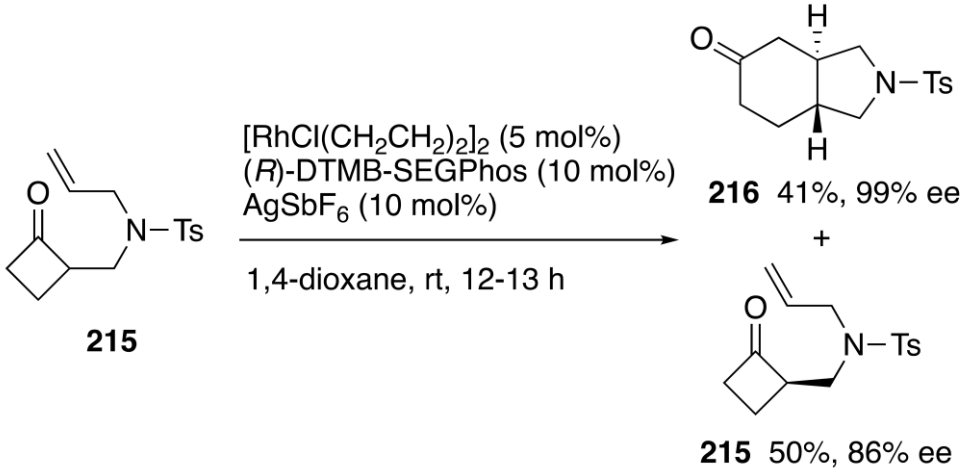




对位变成邻位

Dong, G. *Angew. Chem., Int. Ed*. **2018**, *57*, 2702−2706.

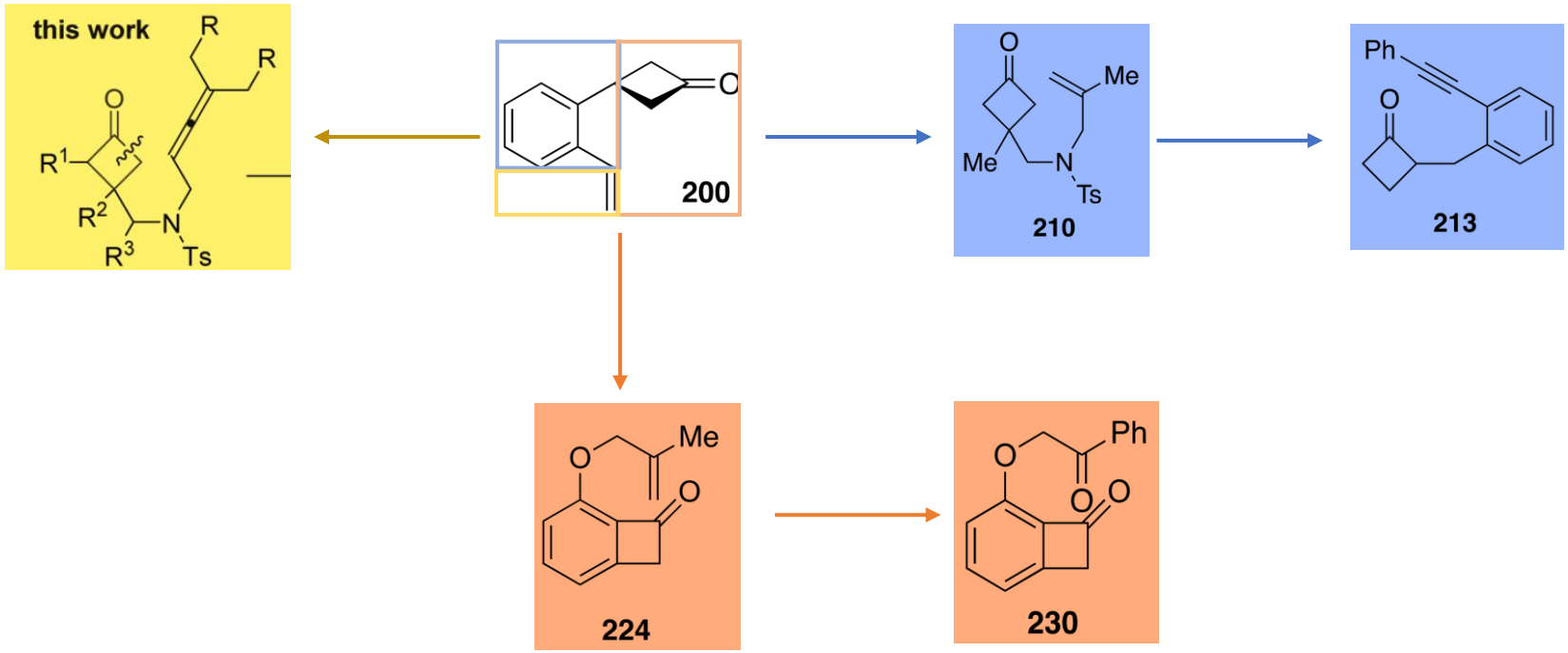
Rhodium Catalysis - Cyclobutanones



邻位首例不对称

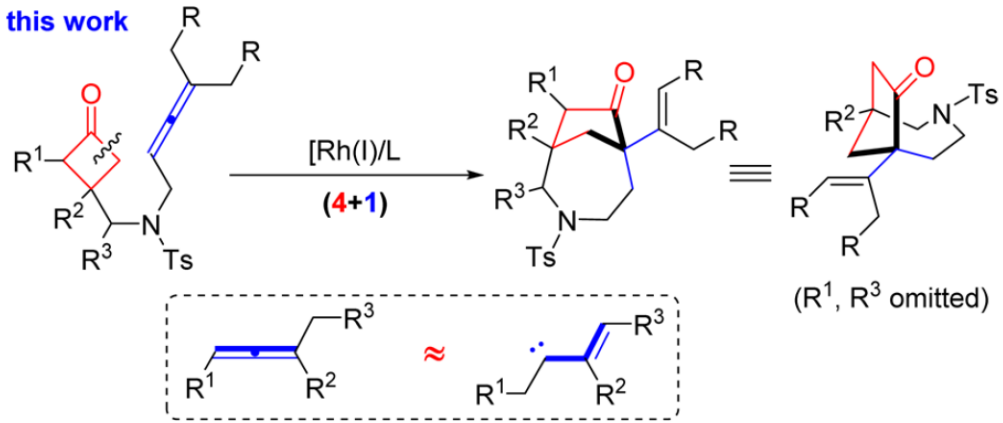
Dong, G.; *J. Am. Chem. Soc.* **2019**, *141*, 16260−16265.

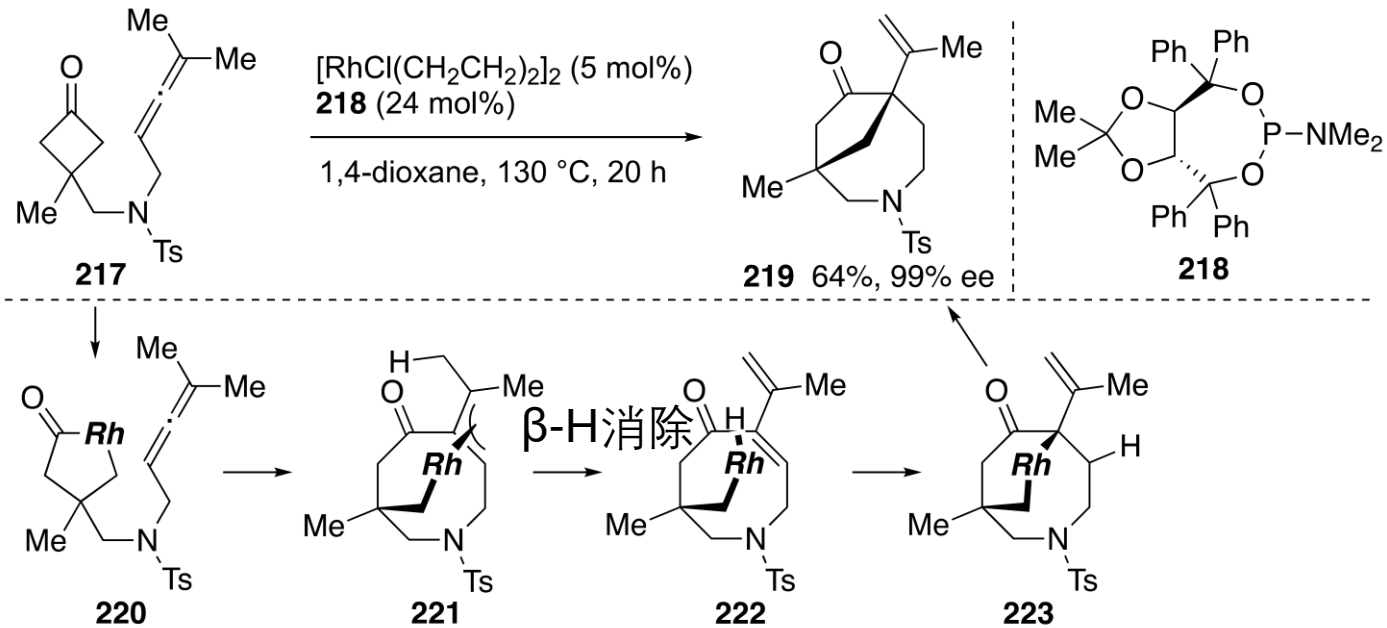
Rhodium Catalysis - process



Rhodium Catalysis - Cyclobutanones

b. allene insertion into C–C bond as a one-carbon unit

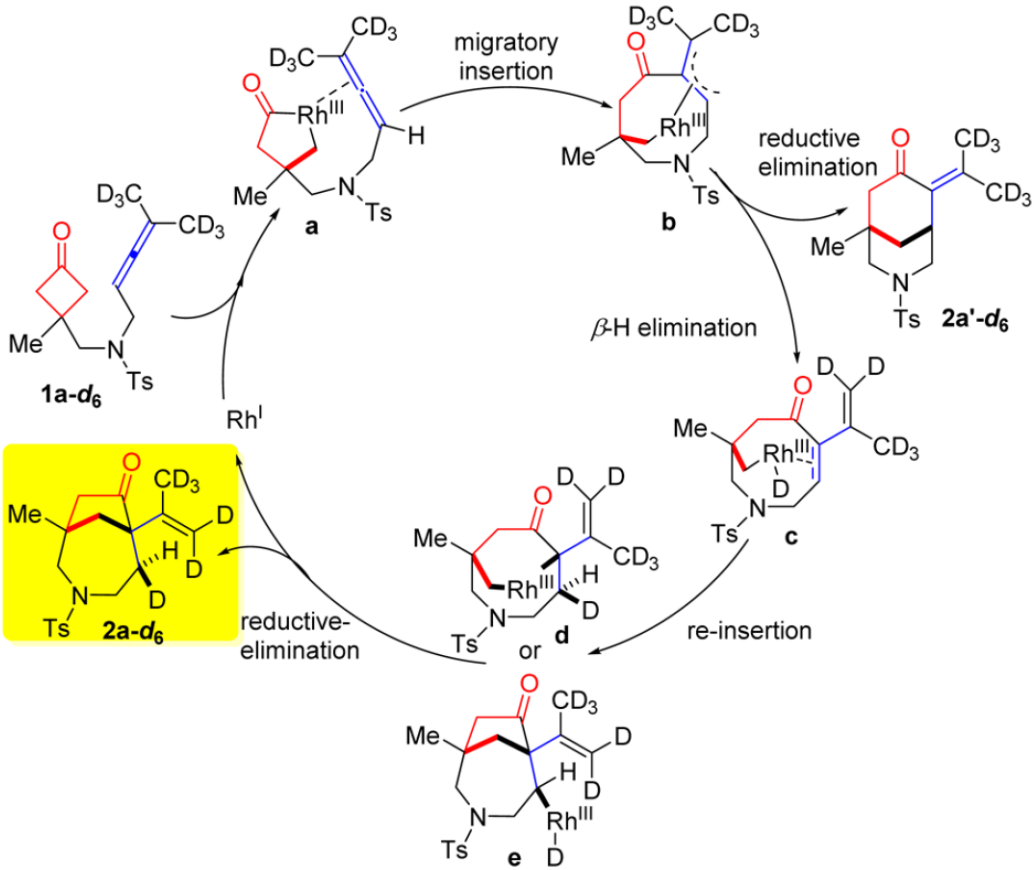




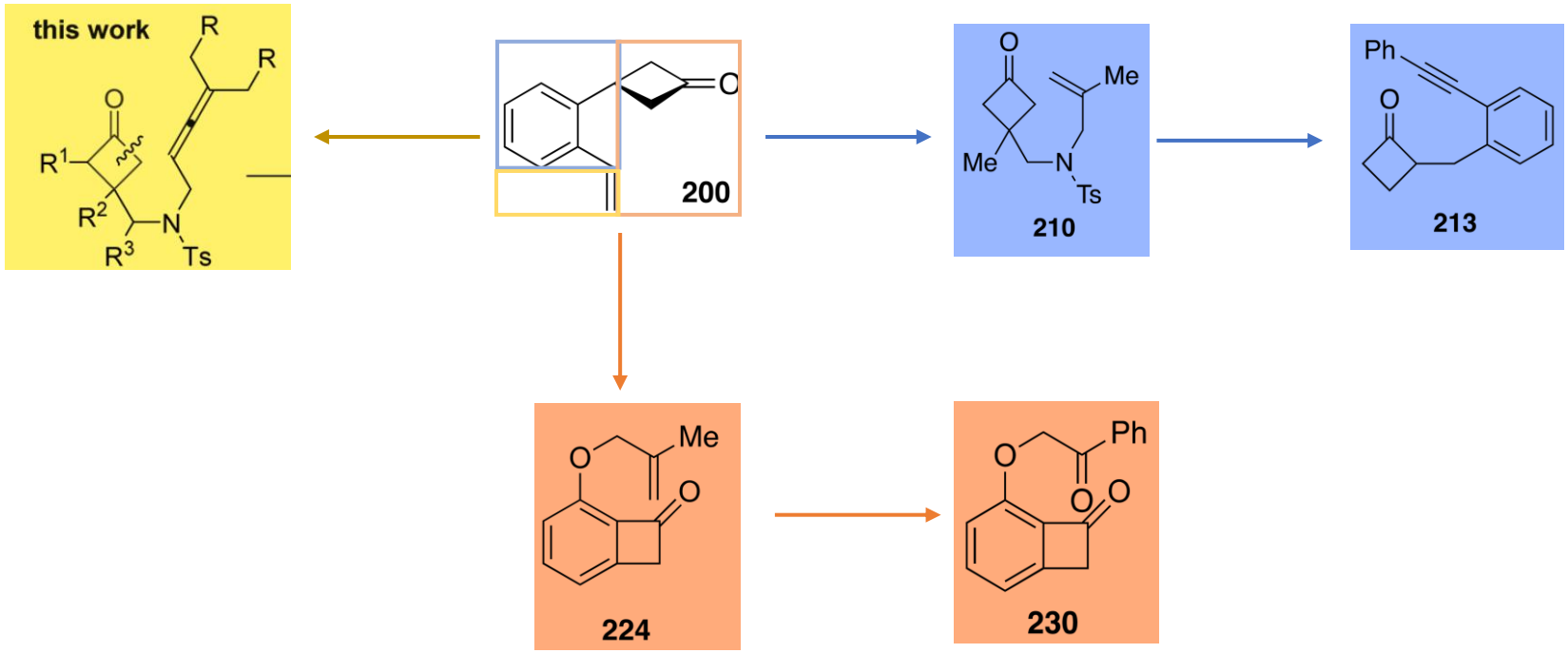
两次迁移插入；连烯作为单碳单元

Dong, G.; *J. Am. Chem. Soc.* 2015, *137*, 13715–13721.

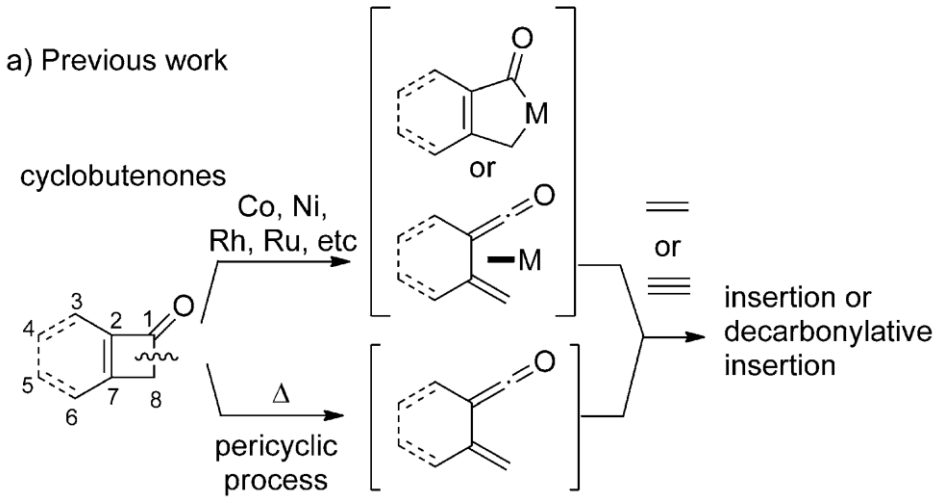
Rhodium Catalysis - Cyclobutanones

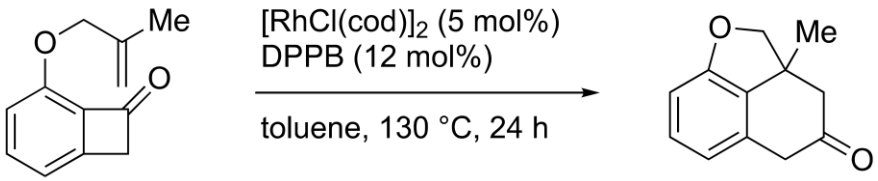


Rhodium Catalysis - process



Rhodium Catalysis - Benzocyclobutanone





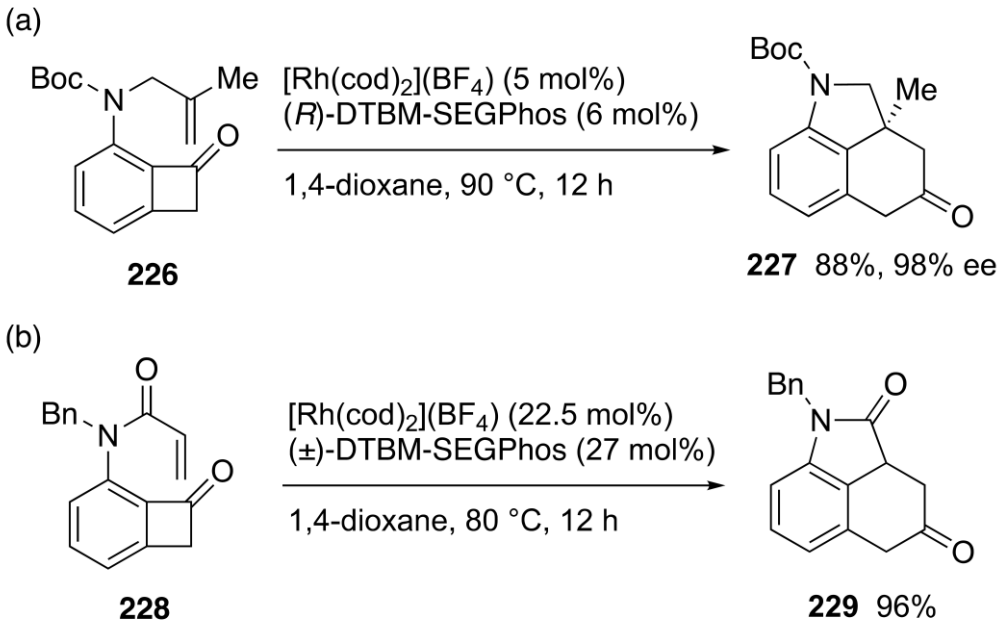
224

225 83%

1,8- C-C活化变成1,2- C-C活化

Dong, G.; *Angew. Chem., Int. Ed*. **2012**, *51*, 7567−7571. *J. Am. Chem. Soc*. **2012**, *134*, 20005−20008

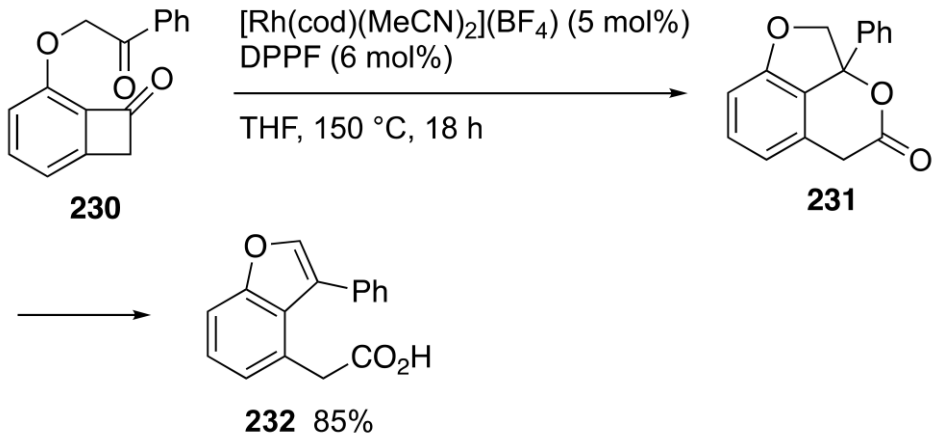
Rhodium Catalysis - Benzocyclobutanone



杂原子氧变成氮

Dong, G.; *J. Am. Chem. Soc.* **2018**, *140*, 9652−9658
Xu, T.; *Org. Lett*. **2018**, *20*, 7689−7693

Rhodium Catalysis - Benzocyclobutanone

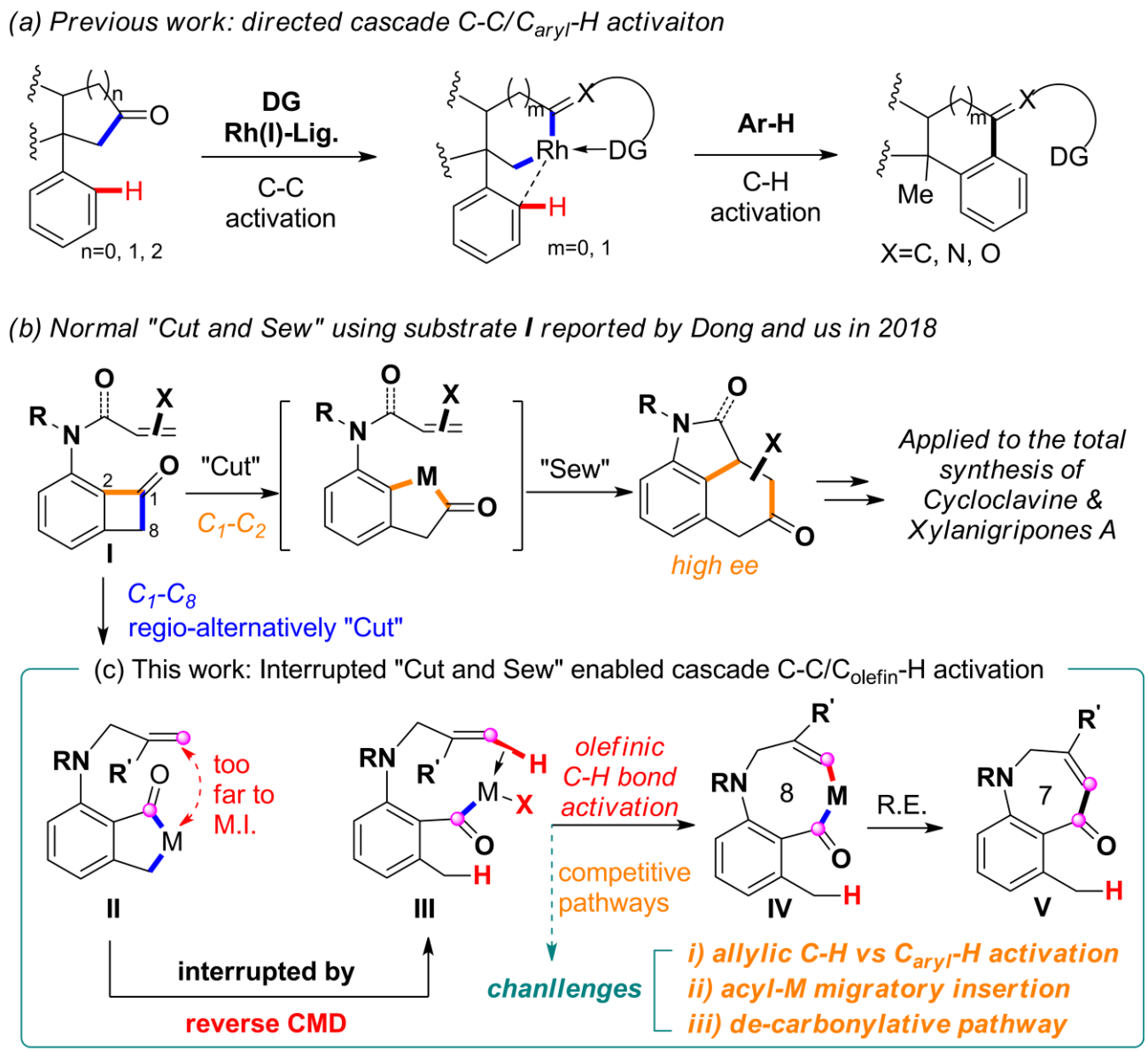


烯烃变成酮

Xu, T. Dong, G.; *Angew.Chem. Int.Ed.* **2018**, *57*,2859 –2863

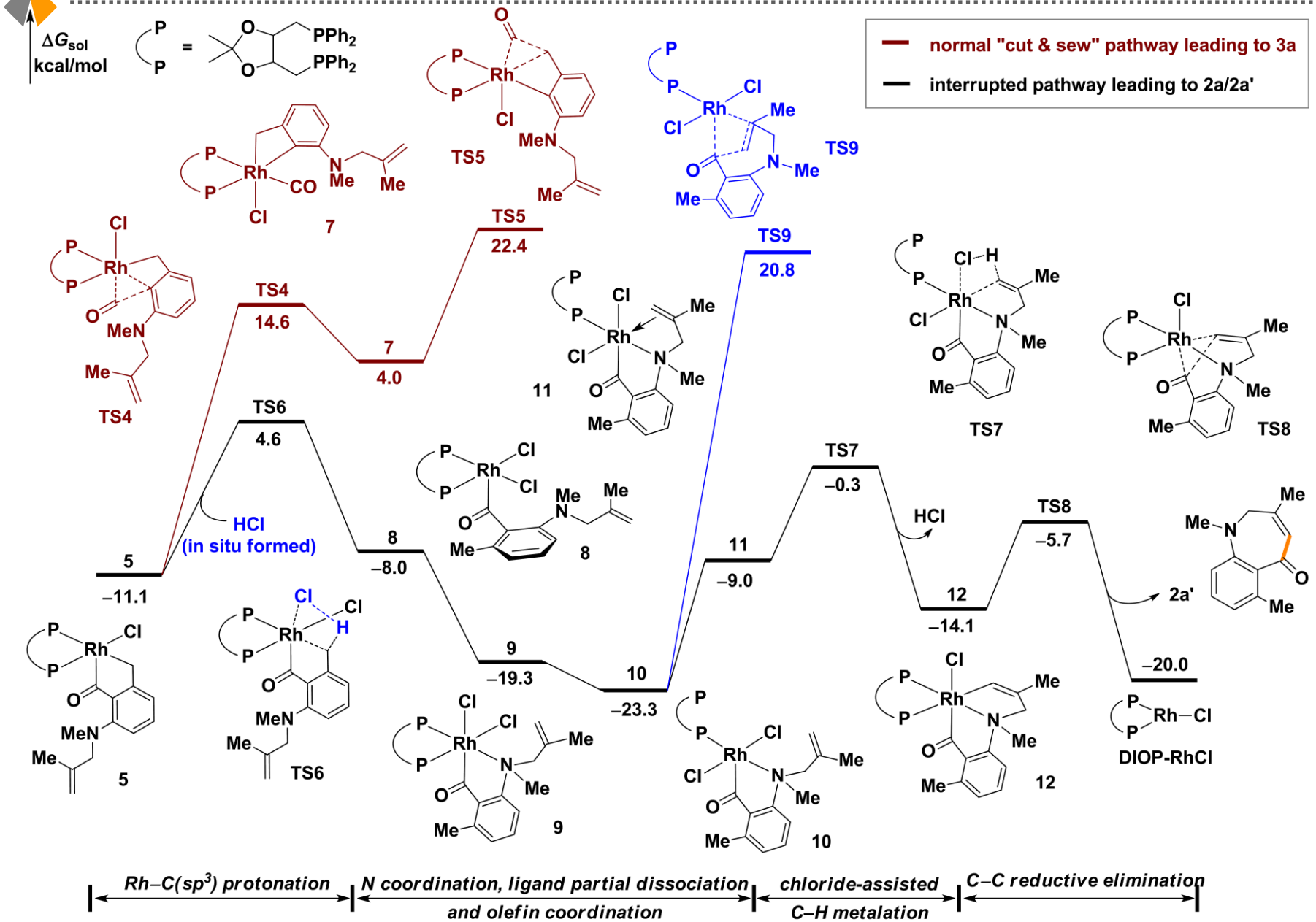
Rhodium Catalysis - process

远端选择性

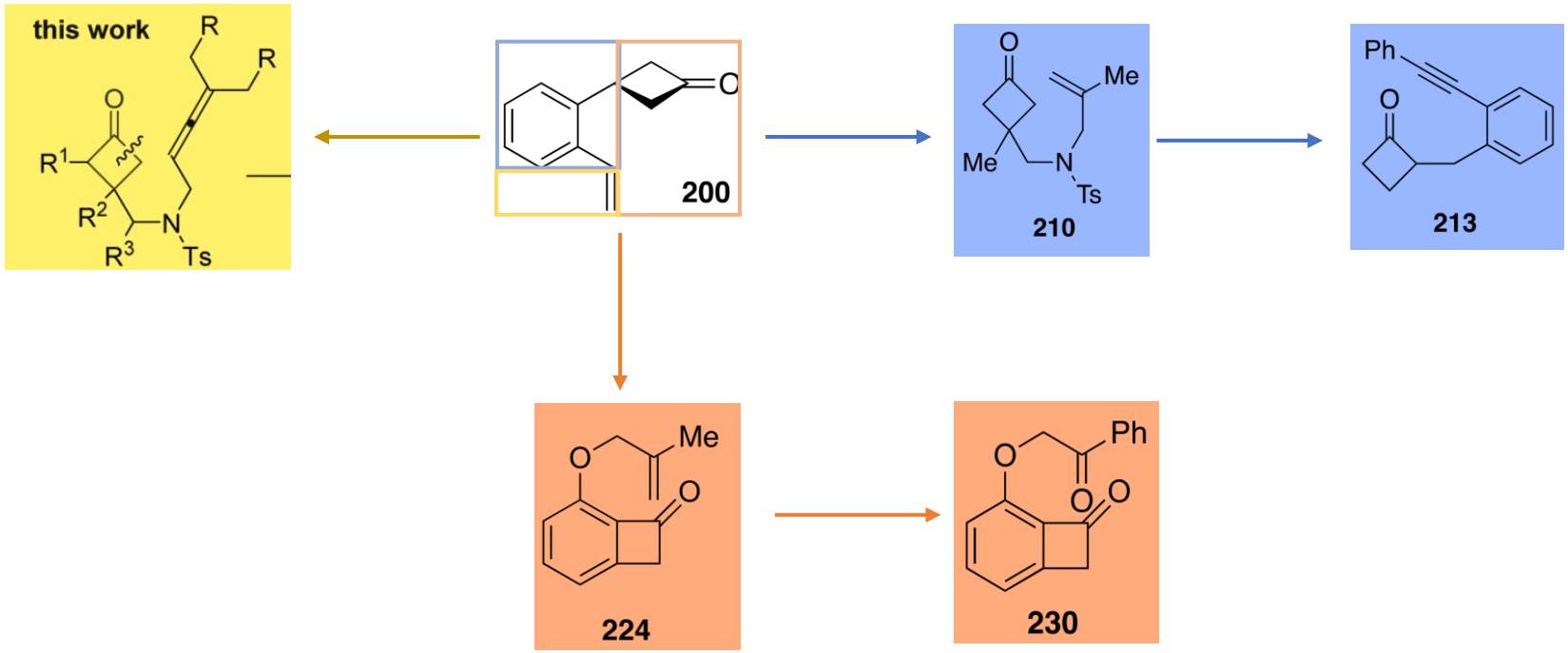


Tao Xu.; *ACS Catal.* **2021**, *11*, 9136−9142

Summary


ΔGsol
kcal/mol
normal "cut & sew" pathway leading to 3a
interrupted pathway leading to 2a/2a'
TS5
22.4
TS9
20.8
TS4
14.6
7
4.0
TS6
4.6
HCl
(in situ formed)
5
–11.1
8
–8.0
9
–19.3
10
–23.3
11
–9.0
TS7
–0.3
HCl
12
–14.1
TS8
–5.7
2a'
–20.0
DIOP-RhCl
Rh–C(sp3) protonation
N coordination, ligand partial dissociation
and olefin coordination
chloride-assisted
C–H metalation
C–C reductive elimination

Rhodium Catalysis - summary



局限:

- 全部为分子内反应，无分子间反应
- 底物中必须包含苯环或者杂原子

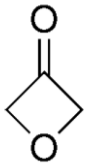
Contents

Nickel Catalysis - *process*

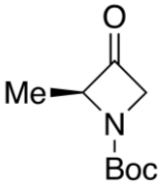
2015
二价镍现场还原成零价镍

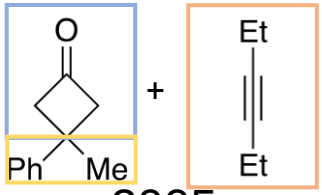
2019
多取代吡啶的合成

2012

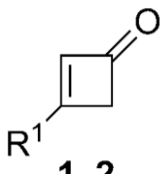


2012-2019





2005



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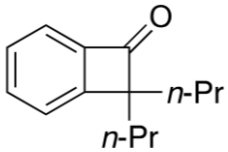
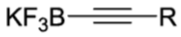


2015



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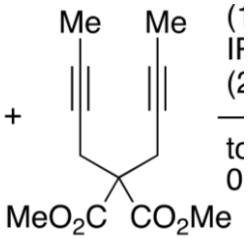

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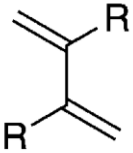

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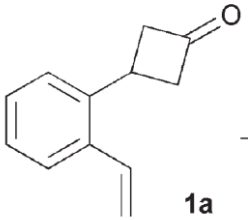

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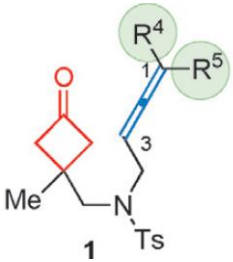
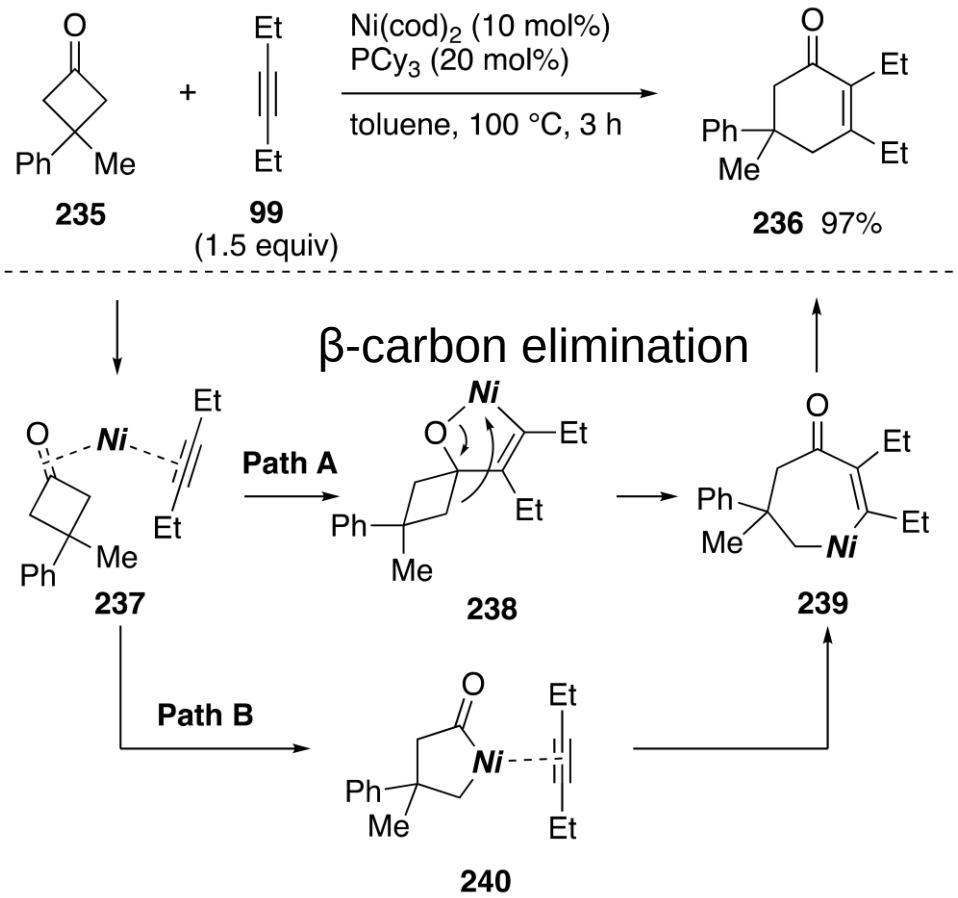


2016

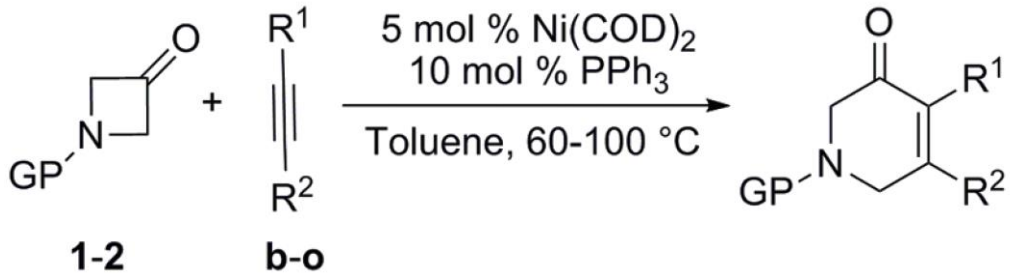
Nickel Catalysis



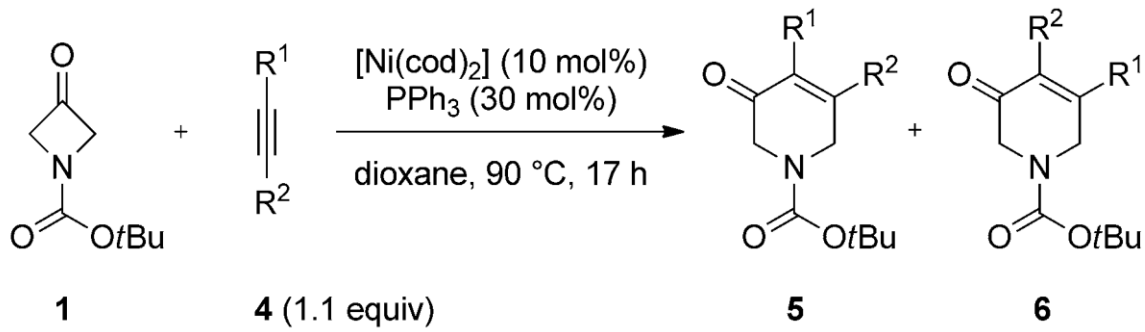
分子间

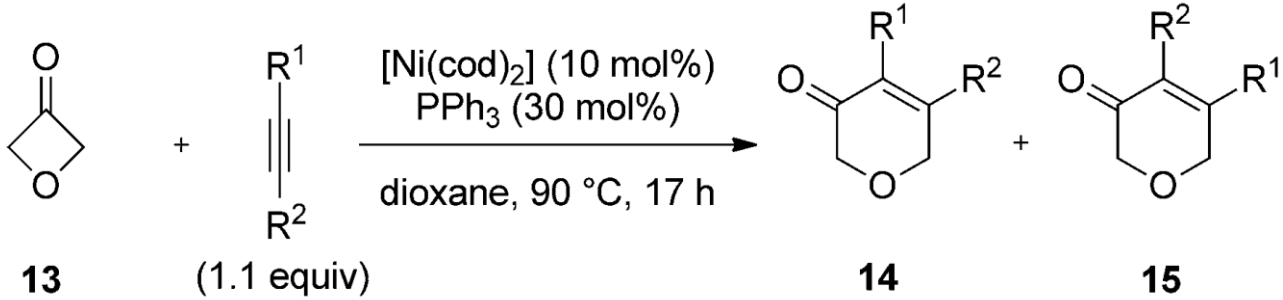
Matsuda, T.; *J. Am. Chem. Soc*. **2005**, *127*, 6932−6933. *Tetrahedron.* **2006**, *62*, 7540−7546.
Zhenyang Lin.; *Organometallics.* **2013**, *32*, 3003−3011.

Nickel Catalysis



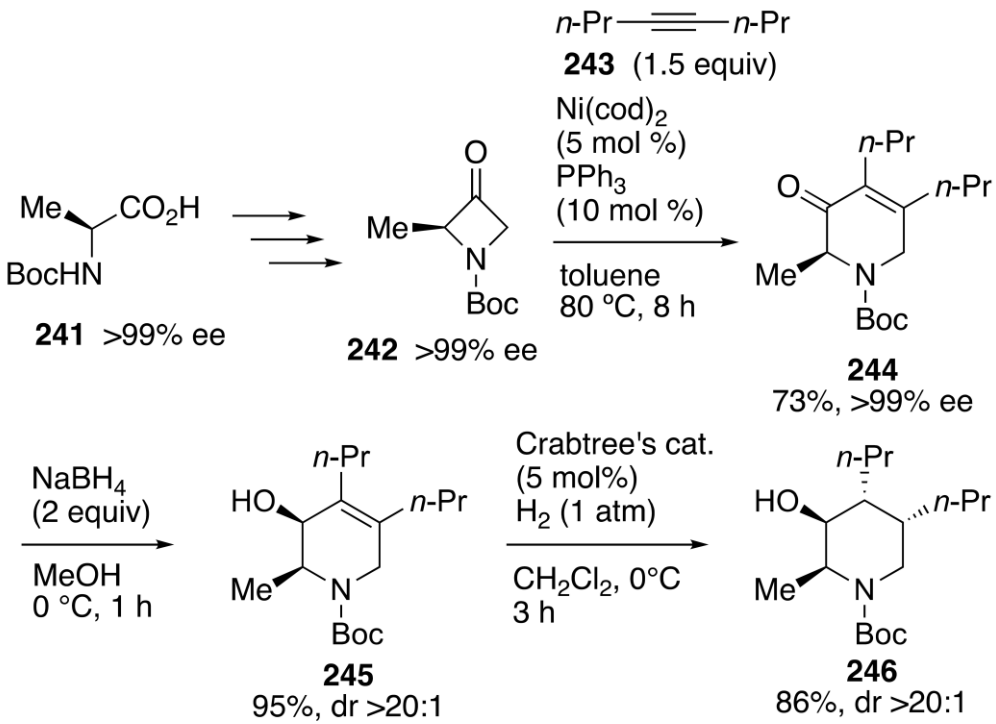
12年以来跟了几篇小文章

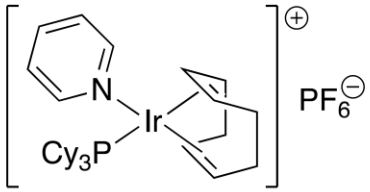




Louie, J.; *Org. Lett.* **2012**, *14*, 2026−2029.
Aïssa, C.; *Chem. - Eur. J.***2012**, *18*, 3486−3489.

Nickel Catalysis

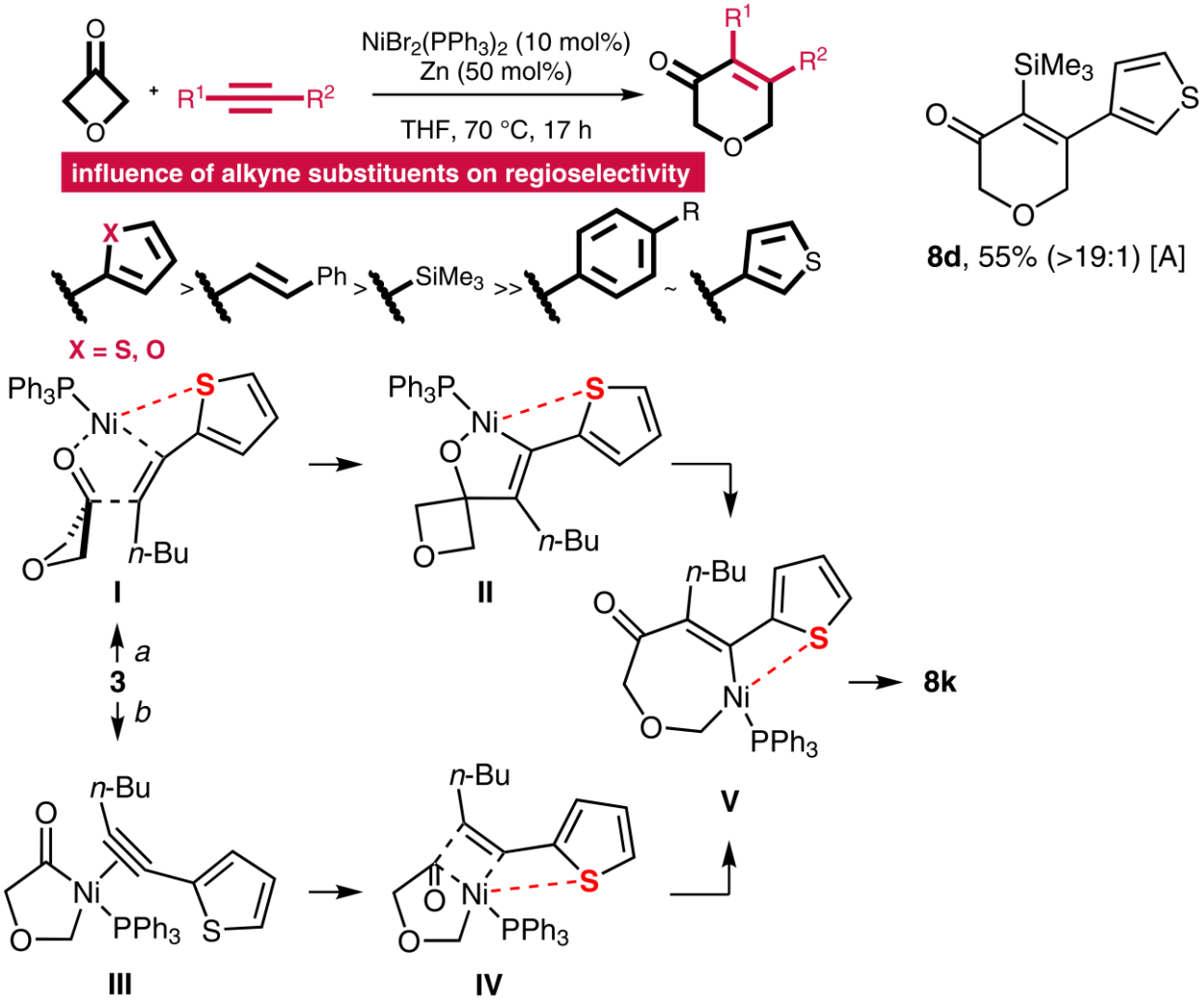




Crabtree's cat.

Murakami, M.; *Org. Lett.* **2012**, *14*, 3898−3901. Louie, J.; *J. Org. Chem*. **2015**, *80*, 9951− 9958. Aïssa, C.; *Org. Lett.* **2016**, *18*, 1756−1659. Aïssa, C.; *Chem. Commun*. **2019,** *55*, 497−500.

Nickel Catalysis

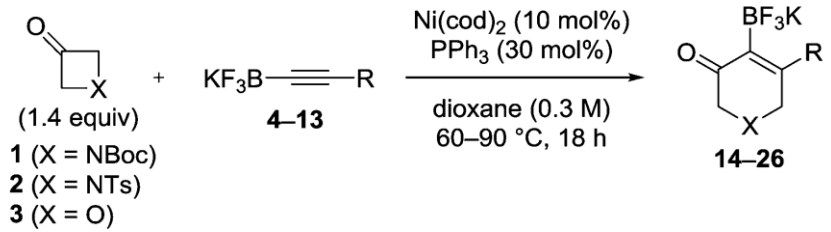


杂原子在区域选择性中的作用

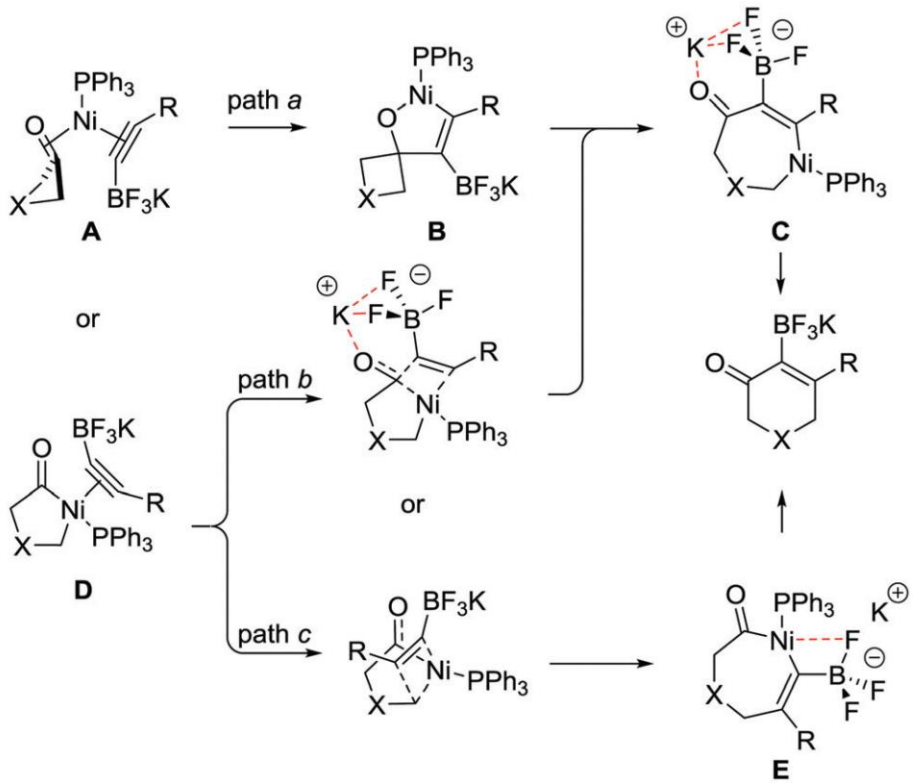
Aïssa, C.; *Synthesis.* **2017**, *49*, 3582−3589.

Nickel Catalysis

C-B键没有断裂



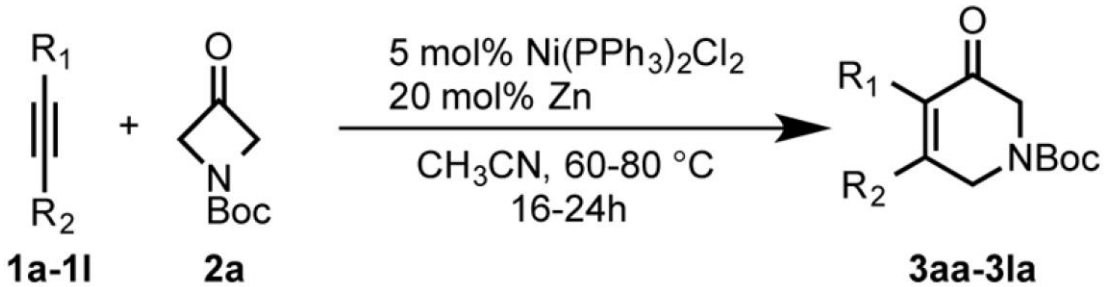
更倾向于path c

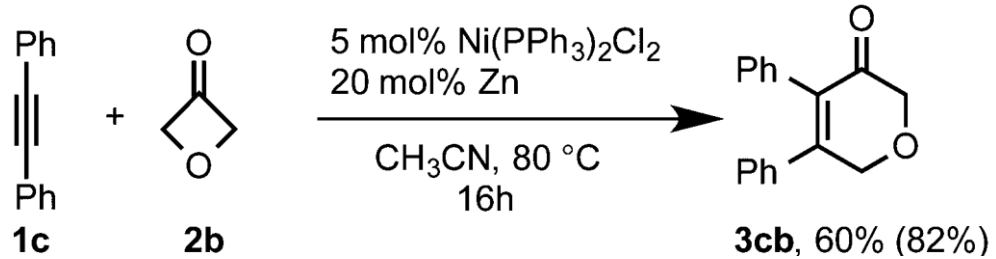


Aïssa, C. *Chem. Commun*. **2019**, *55*, 497−500.

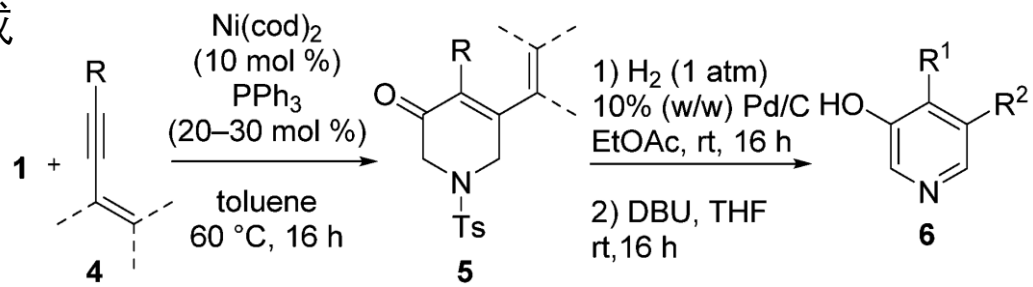
Nickel Catalysis

二价镍现场还原成零价镍



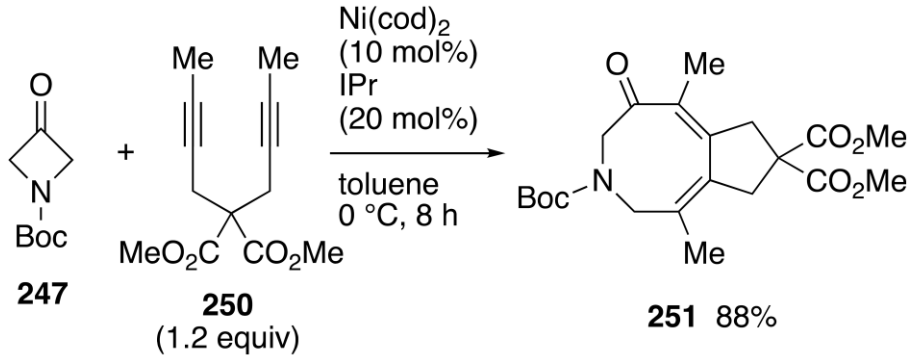


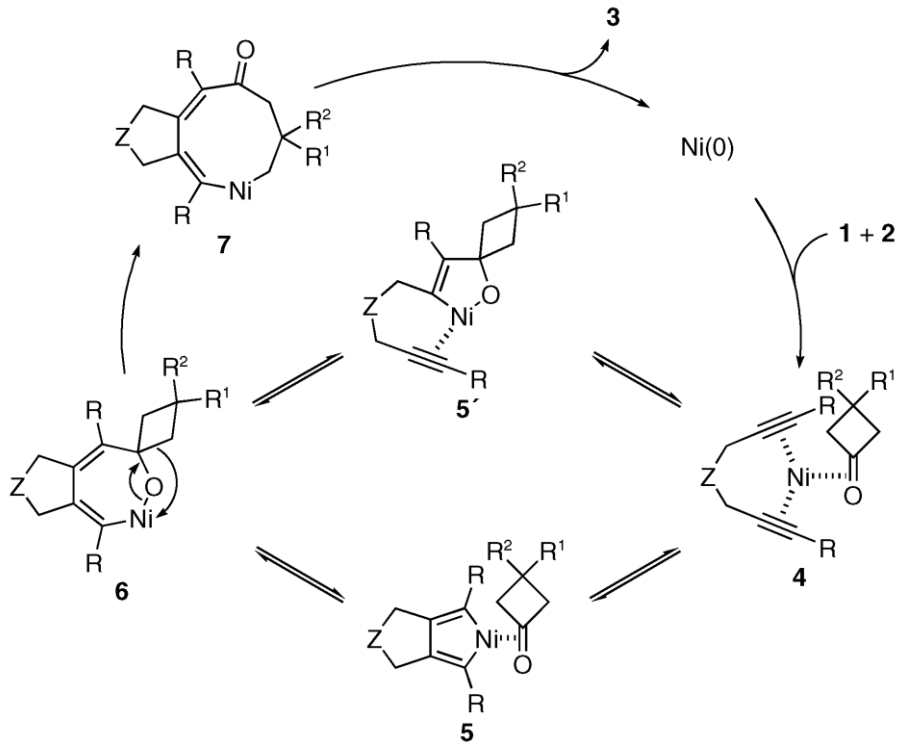
多取代吡啶的合成



Louie, J.; *J. Org. Chem.* **2015**, *80*, 9951−9958. Aïssa, C.; *Org. Lett*. **2016**, *18*, 1756−1659.
Aïssa, C.; *Chem. Commun*. **2019**, *55*, 497−500.

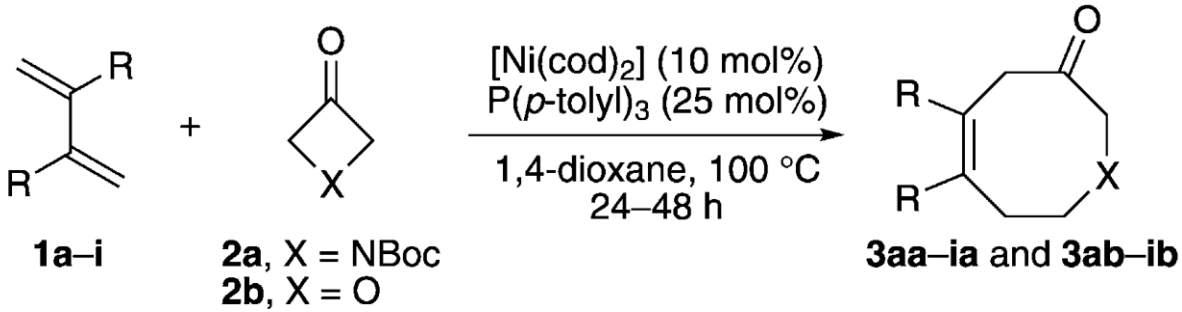
Nickel Catalysis

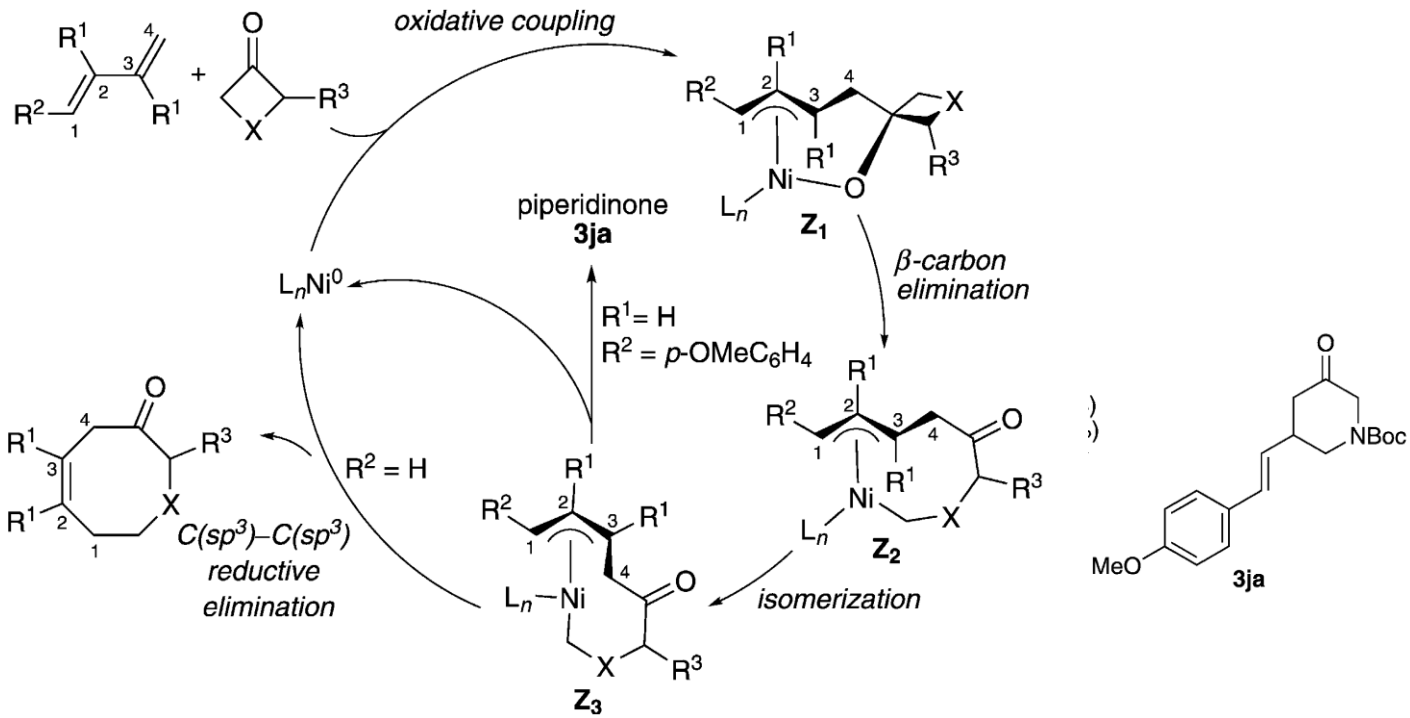




Matsuda, T.; *J. Am. Chem. Soc*. **2006**, *128*, 2166−2167.
Murakami, M.; *Bull. Chem. Soc. Jpn*. **2008**, *81*, 885−893.
Louie, J.; *Angew. Chem., Int. Ed*. **2012**, *51*, 8602−8606.

Nickel Catalysis



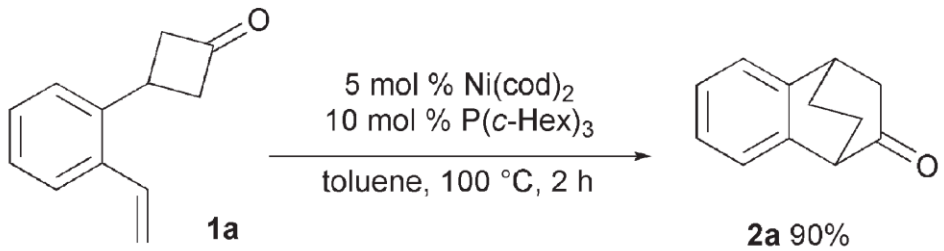


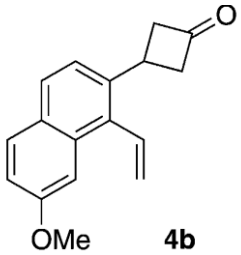
炔烃拓成二烯

Louie, J.; *Angew. Chem., Int. Ed.* **2013**, *52*, 12161−12165.

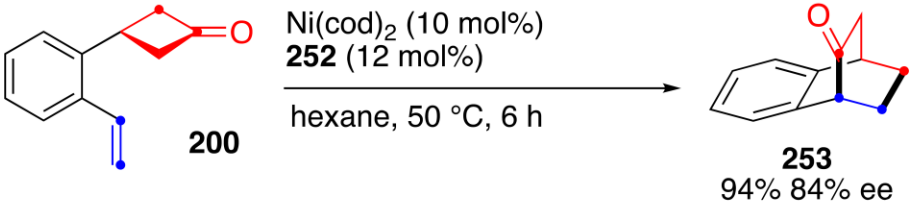
Nickel Catalysis

首例炔烃拓成烯烃

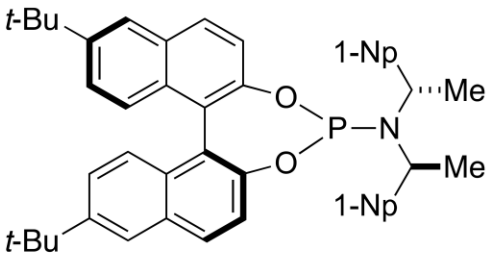




RT, 84%, 92 ee%



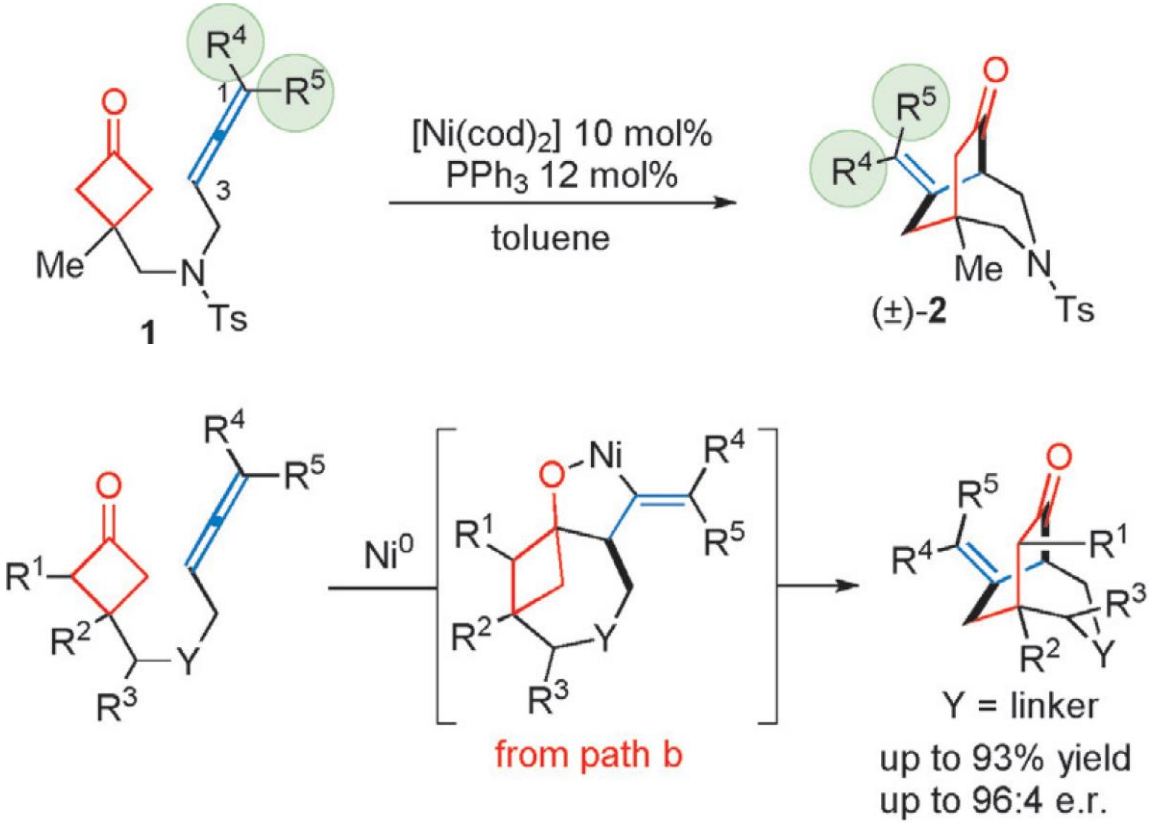
首例不对称
苯环换成萘基活性更高



252

Ashida, S.; *Chem. Commun*. **2006**, *44*, 4599−4601.
Murakami, M.; *Angew. Chem., Int. Ed*. **2012**, *51*, 2485−2488.

Nickel Catalysis

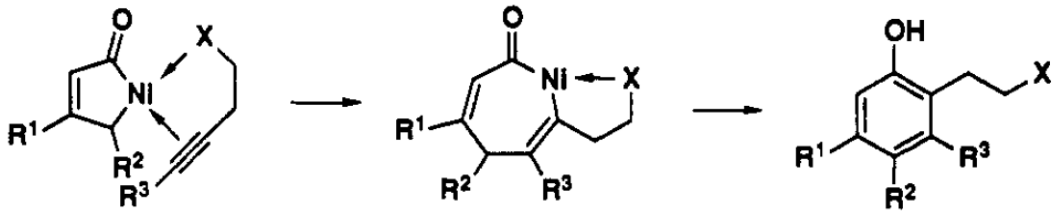


引入杂原子，炔烃拓成连烯

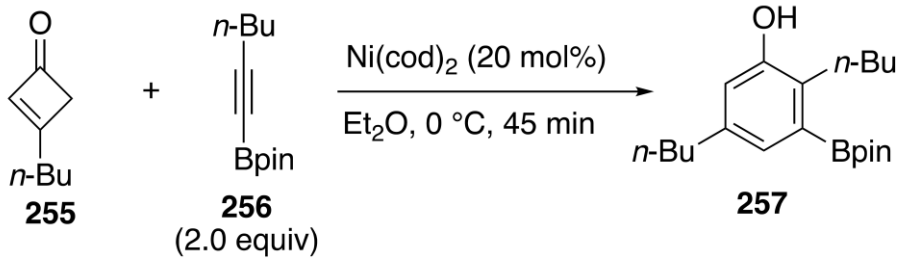
Dong, G.; *Angew. Chem., Int. Ed*. **2016**, *55*, 15091− 15095.

Nickel Catalysis

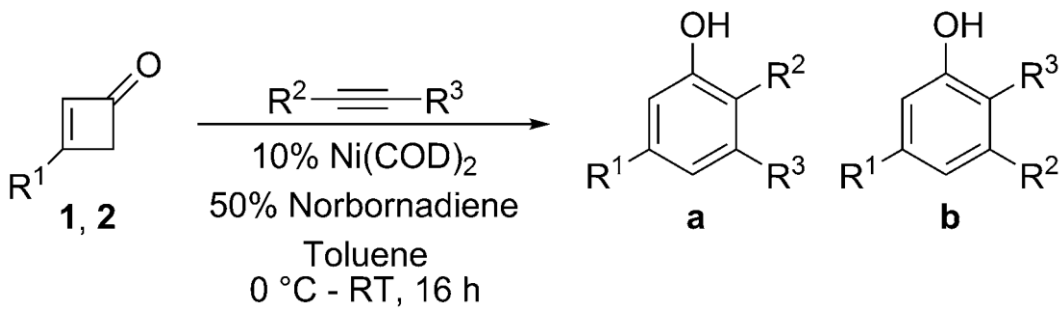
首例发现在1991年



杂原子B是必须



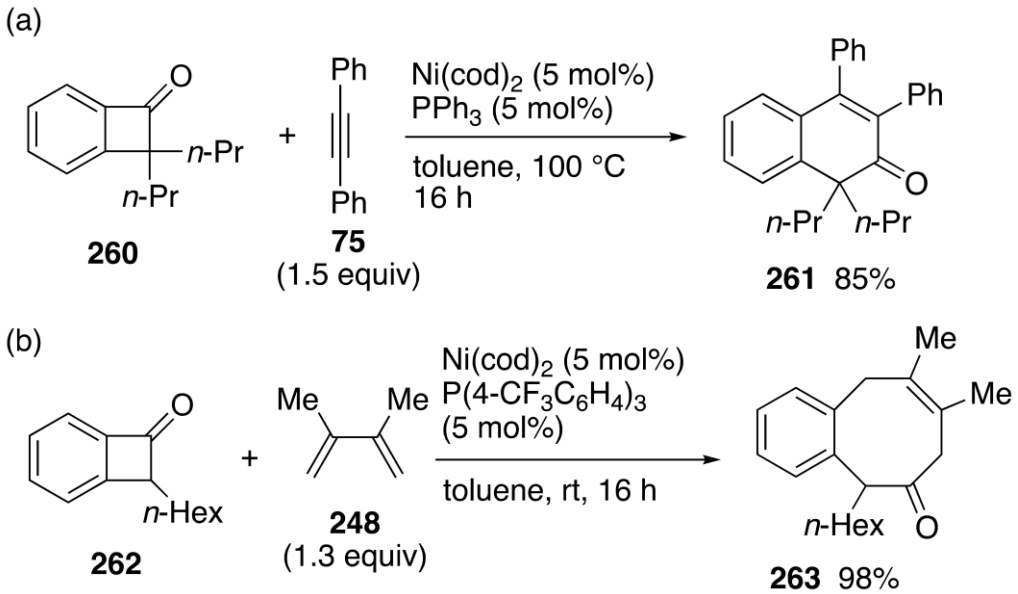
普通炔烃



Norbornadiene

Liebeskind, L. S.; *J. Am. Chem. Soc.* **1991**, *113*, 2771−2772.
Harrity, J. P. A.; *Angew. Chem., Int. Ed.* **2011**, *50,* 2769−2772.
Cornel, E. J.; *Chem. - Eur. J.* **2015**, *21*, 2701−2704.

Nickel Catalysis



苯并环丁酮

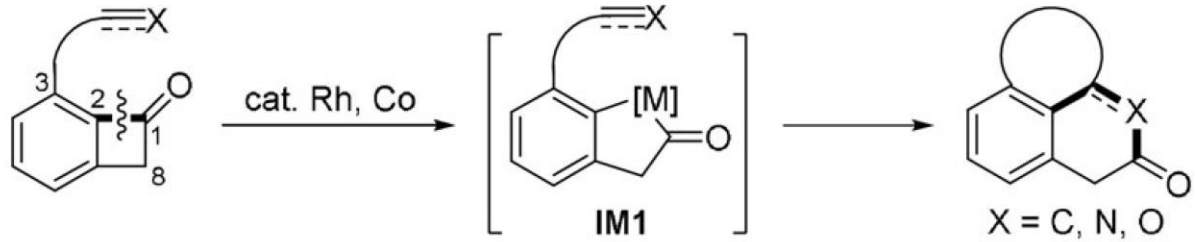
Martin, R.; *Angew. Chem., Int. Ed.* **2015**, *54*, 9537−9541.

Nickel Catalysis

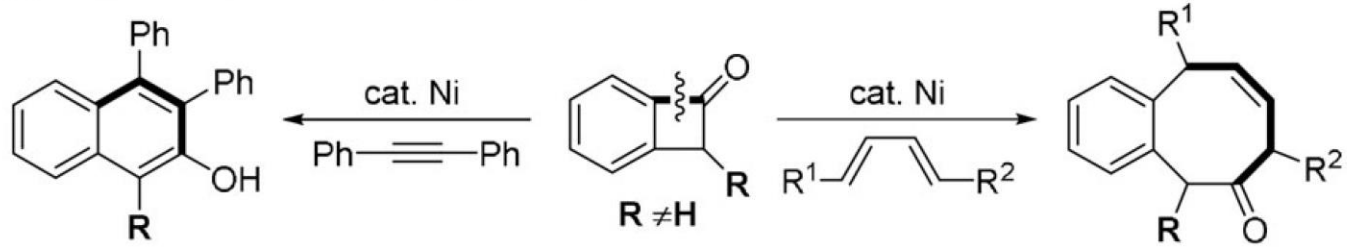
远端选择性

Previous work: Reactions of BCBs with 2π units through C1–C2 bond cleavage

(a) Intramolecular reactions (by Dong)

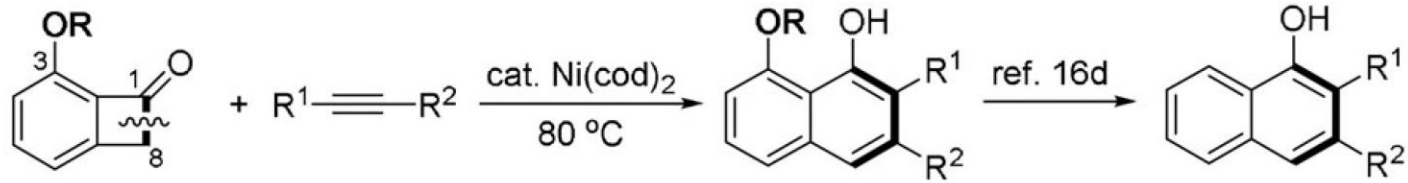


(b) Intermolecular reactions (by Martin)



This work:

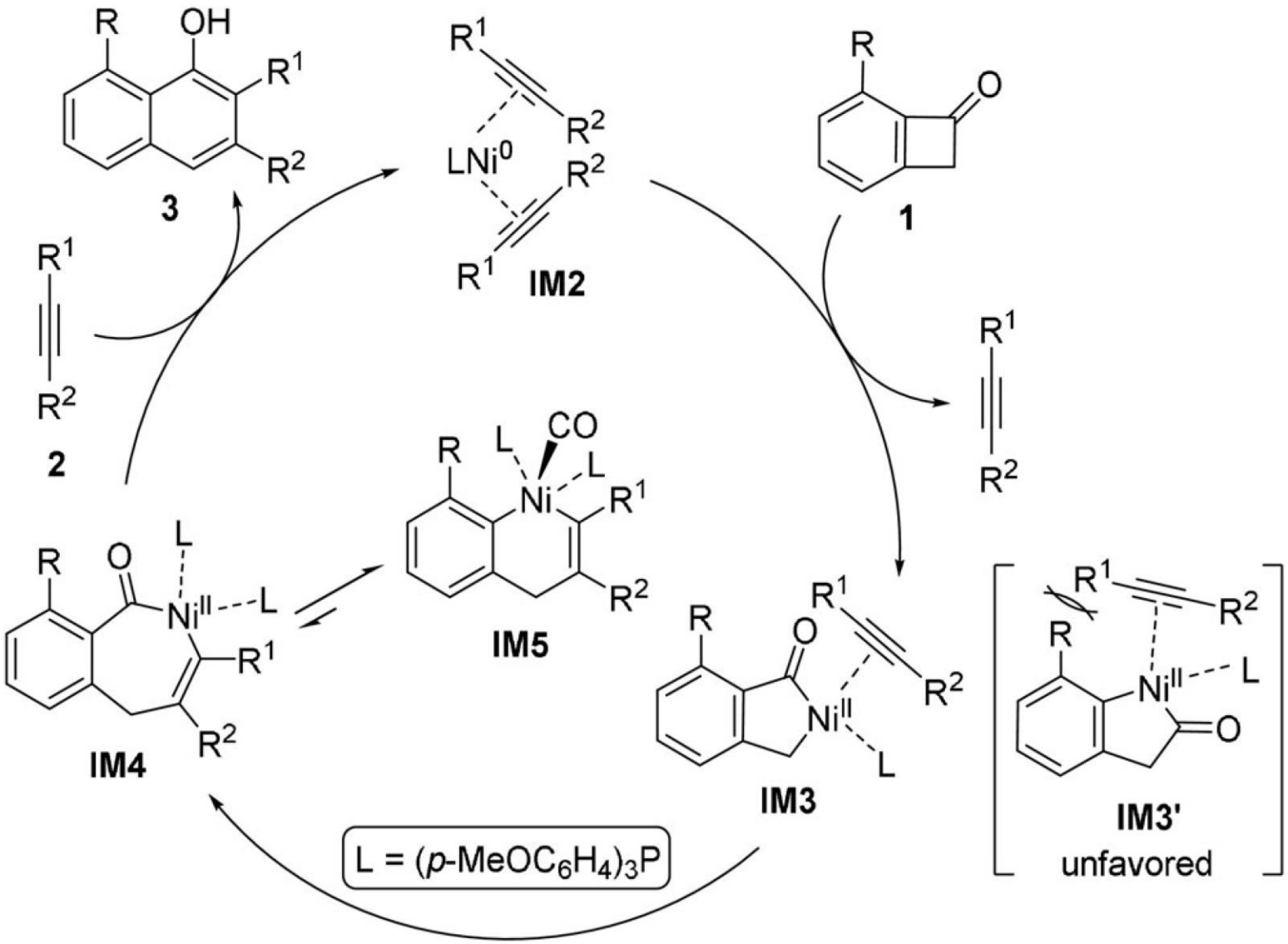
(c) Sterically-controlled C1–C8 bond cleavage of BCBs



- *unconventional regioselectivity*
- *neutral reaction condition*
- *high atom and step economies*
- *mechanistic studies*

Zhang-Jie Shi.; *Angew. Chem. Int. Ed.* **2021**, *60*, 1 – 7

Summary

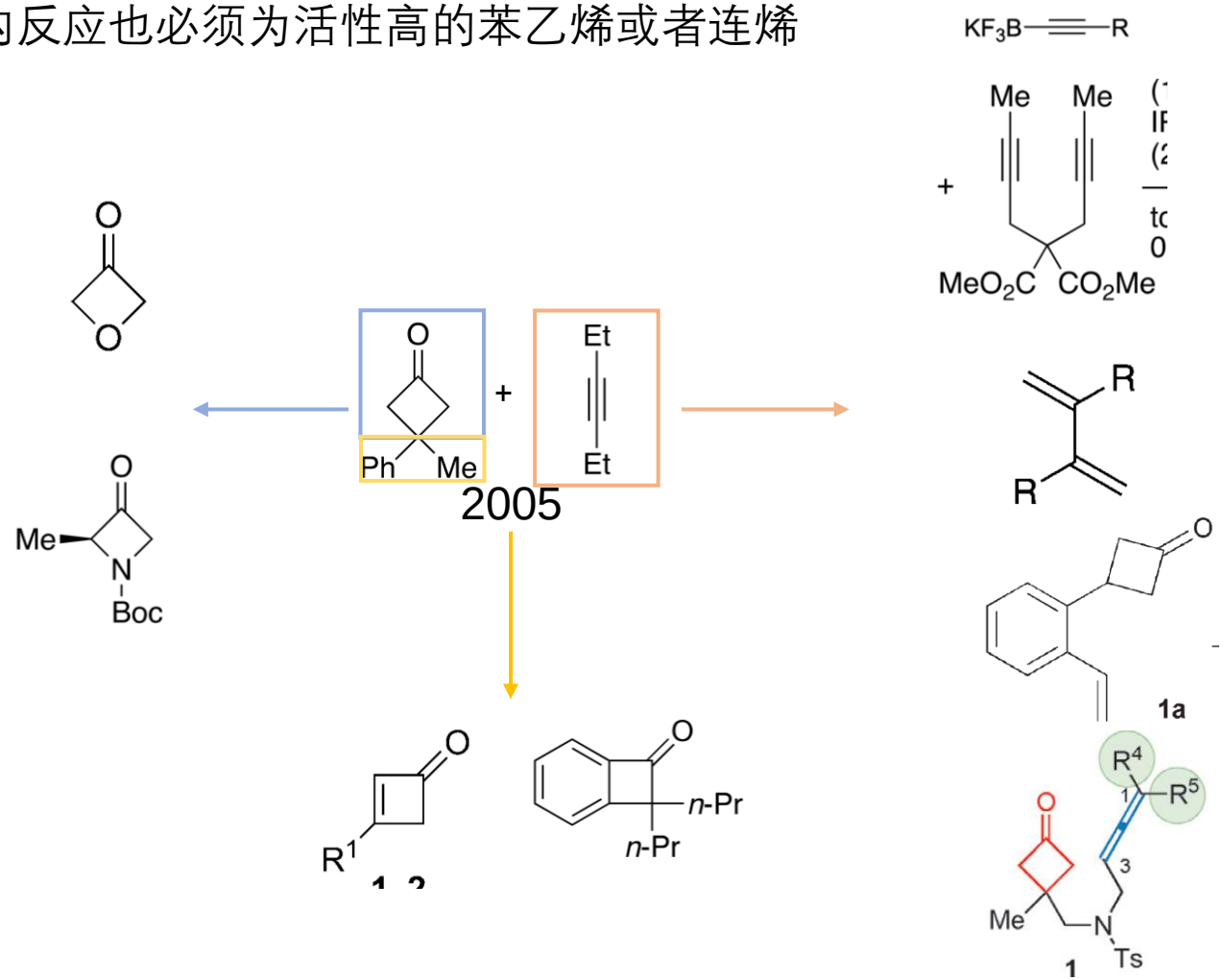

R
OH
R1
R2
3
R1
R2
LNi0
R2
R1
IM2
R
O
1
R1
R2
2
R1
R2
R
L
CO
L
Ni
R1
R2
IM5
R
O
L
NiII
L
R1
R2
IM4
R
O
R1
R2
NiII
L
IM3
R1
R2
R
NiII
L
O
IM3'
unfavored
L = (p-MeOC6H4)3P

Nickel Catalysis - *summary*

局限:

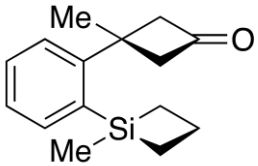
- 没有一例不对称
- 分子间反应必须为活性高的炔烃或者二烯,

分子内反应也必须为活性高的苯乙烯或者连烯

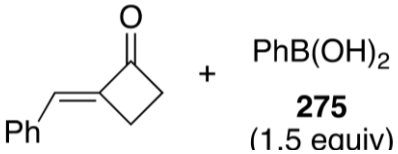


Contents

Palladium Catalysis - *process*

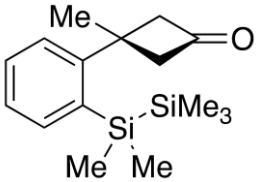


2014



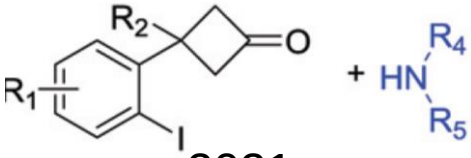
2016

转金属

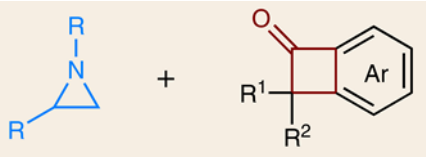


2012

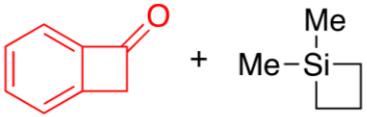
其它



2021

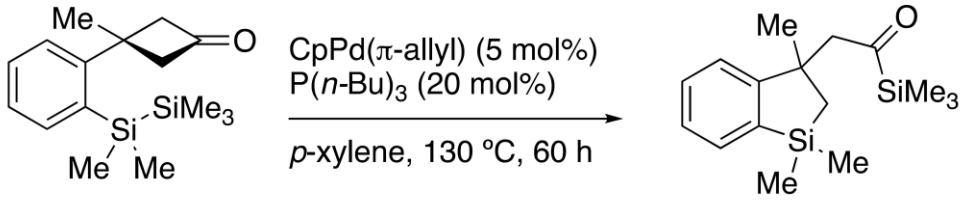


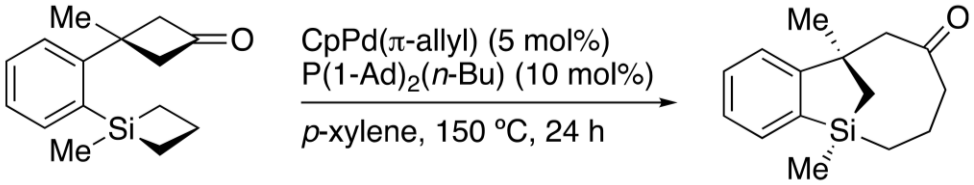
2021



2017

Palladium Catalysis

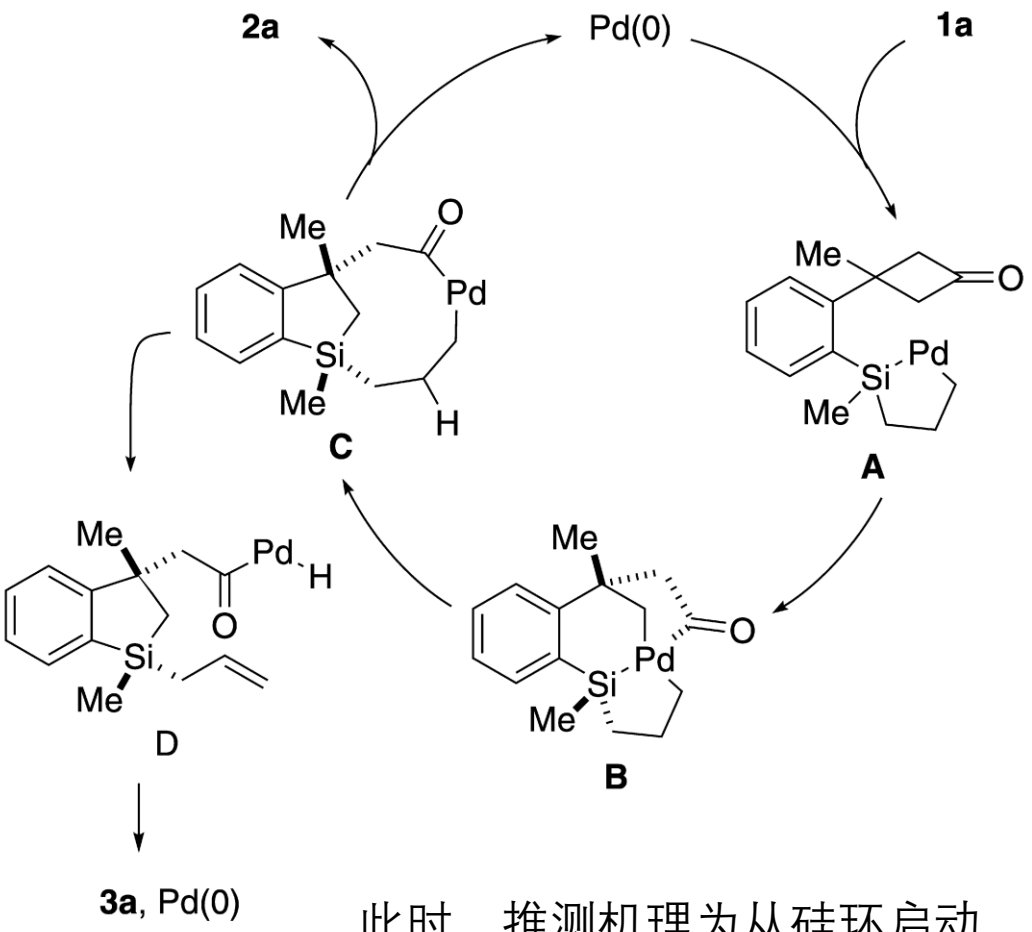




270 **271** 86%

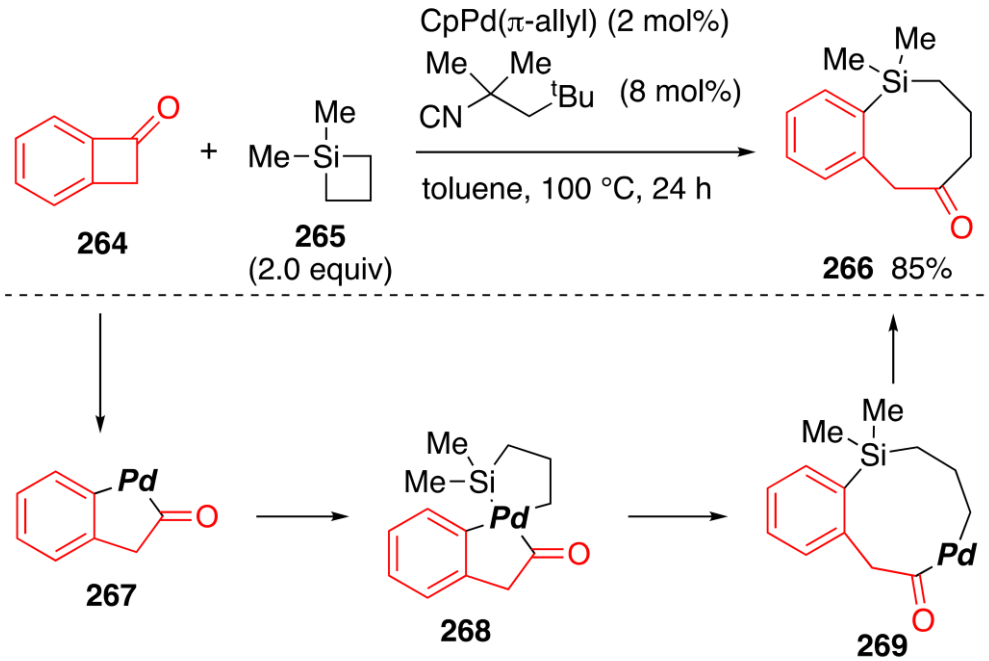
Murakami, M.; *Org.Lett.* **2012**, *14*, 3230−3232.
Murakami, M.; *J. Am. Chem. Soc.* **2014**, *136*, 5912−5915.

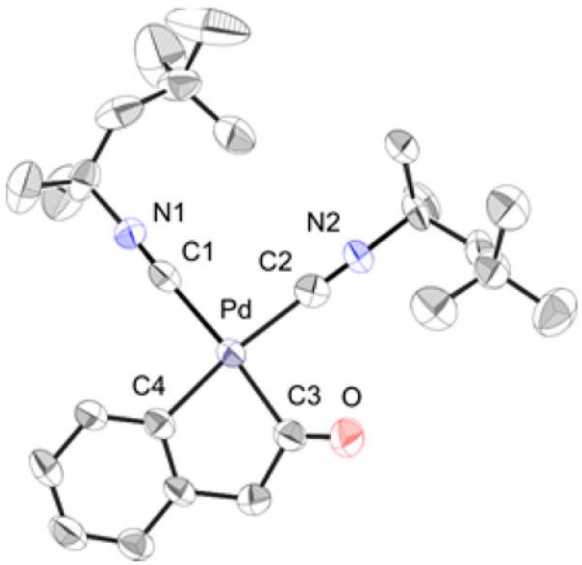
Palladium Catalysis



此时，推测机理为从硅环启动

Palladium Catalysis

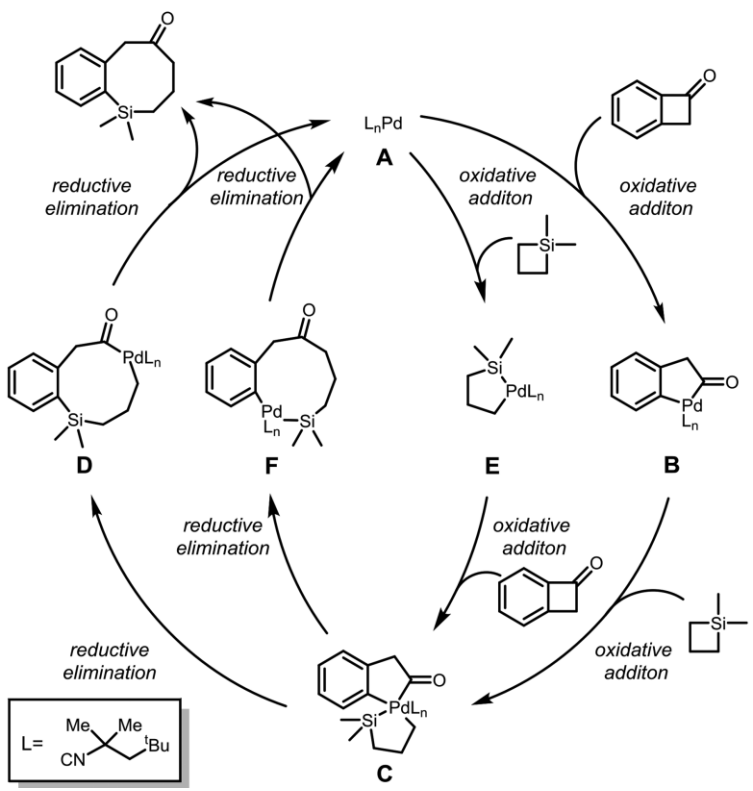


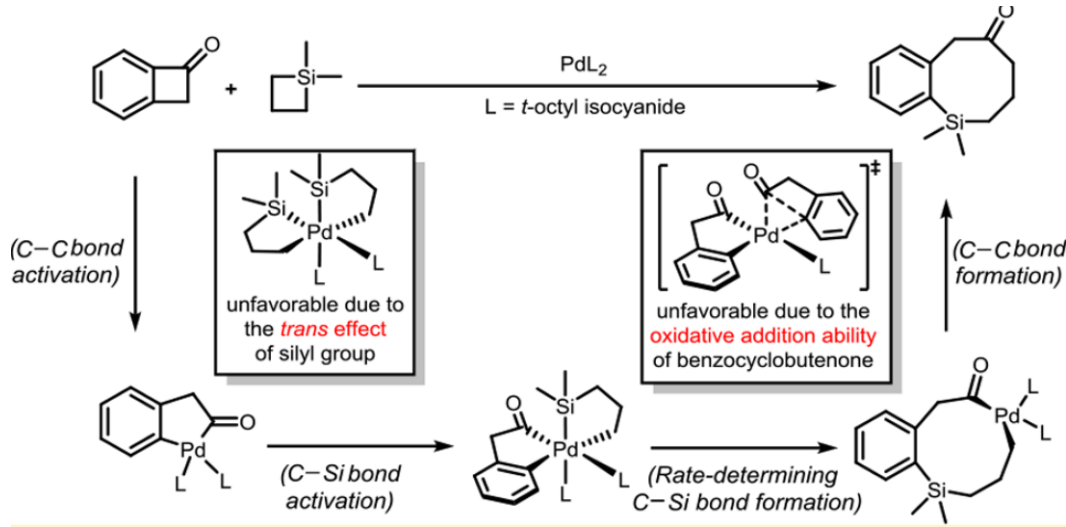


通过单晶提出从C-C键启动

Murakami, M.; *J. Am. Chem. Soc.* **2017**, *139*, 12414−12417.

Palladium Catalysis



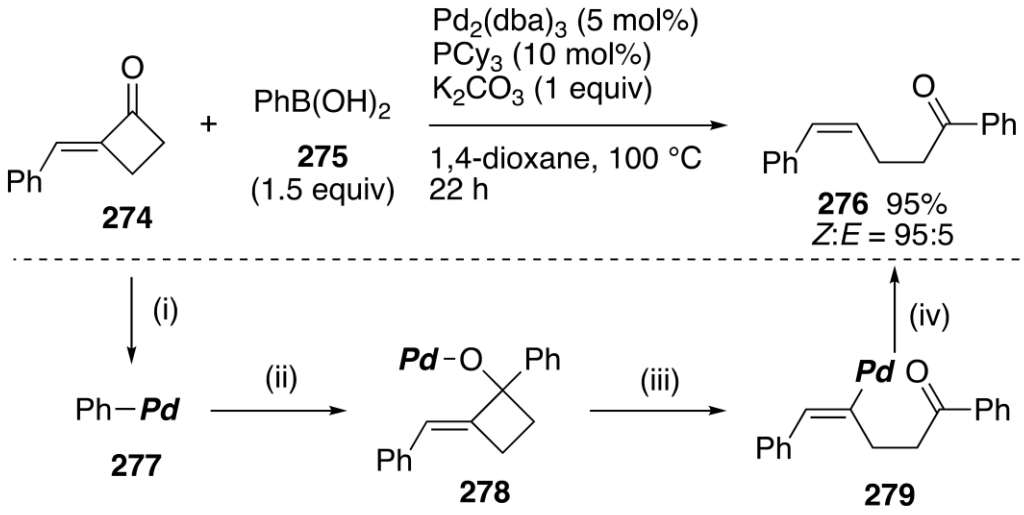


计算表明从C-C键启动可能性更大

Yao Fu.; *Organometallics.* **2018**, *37*, 592−602.

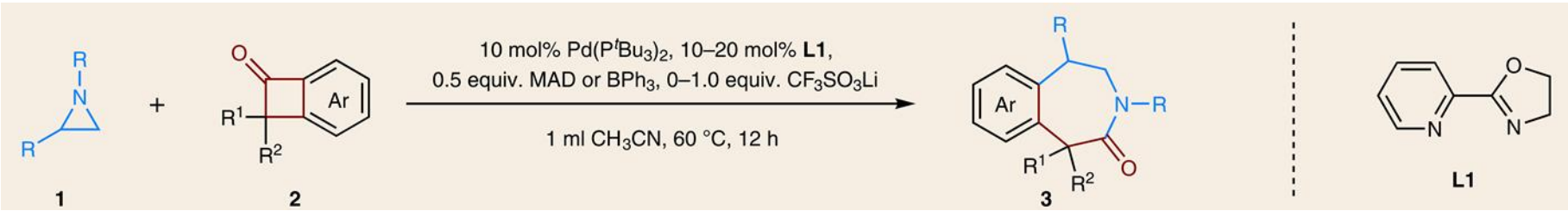
Palladium Catalysis

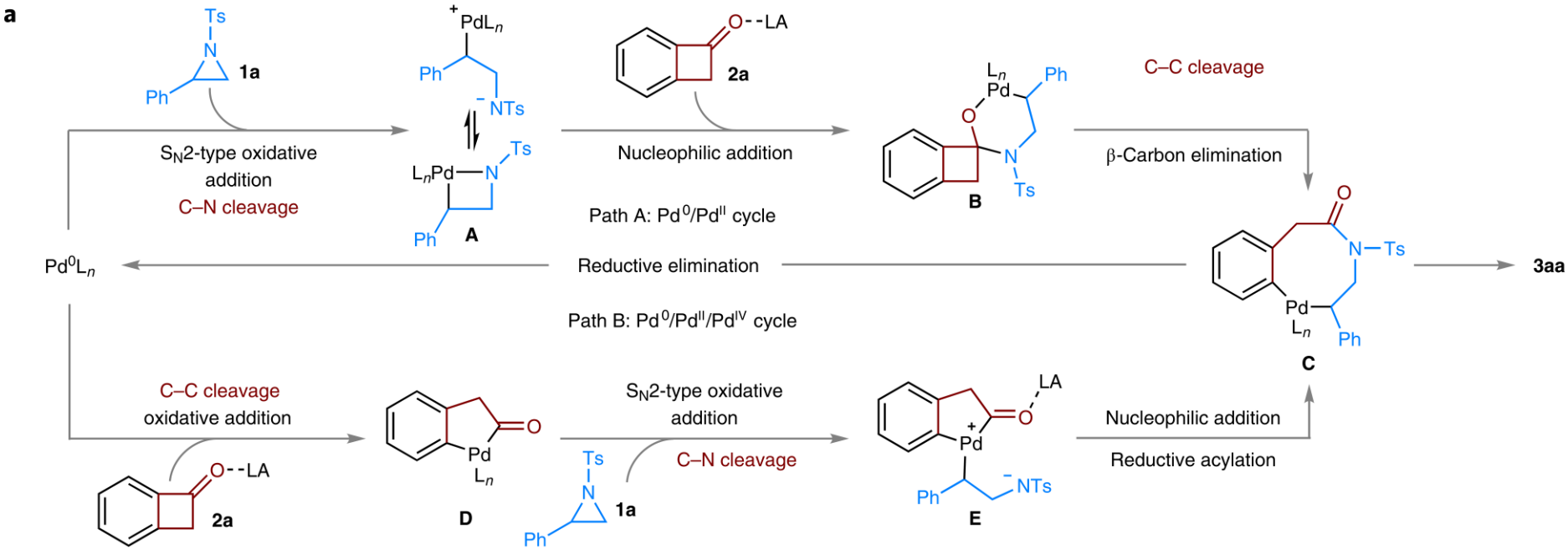
提出的机理类似于Murakami 在2012年和2014年提出的从Si-Si或C-Si启动，是不是还存在从C-C键启动的可能性



Song, Q. *Org. Lett.* **2016**, *18*, 4000−4003.

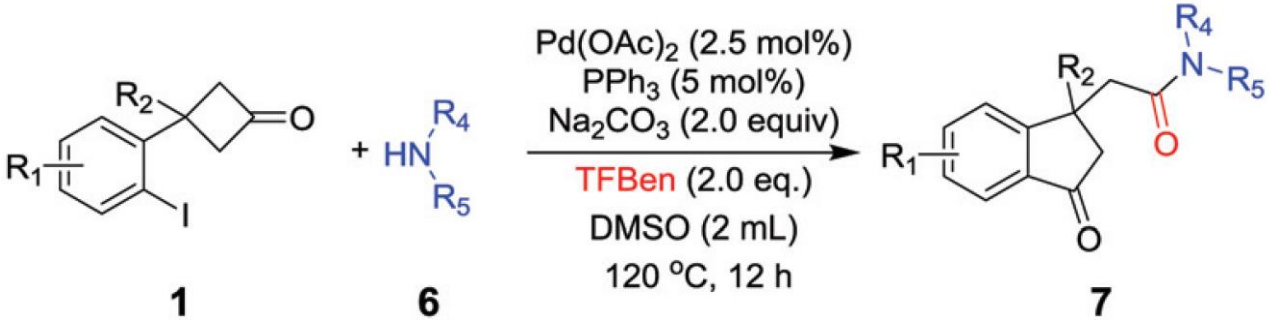
Palladium Catalysis

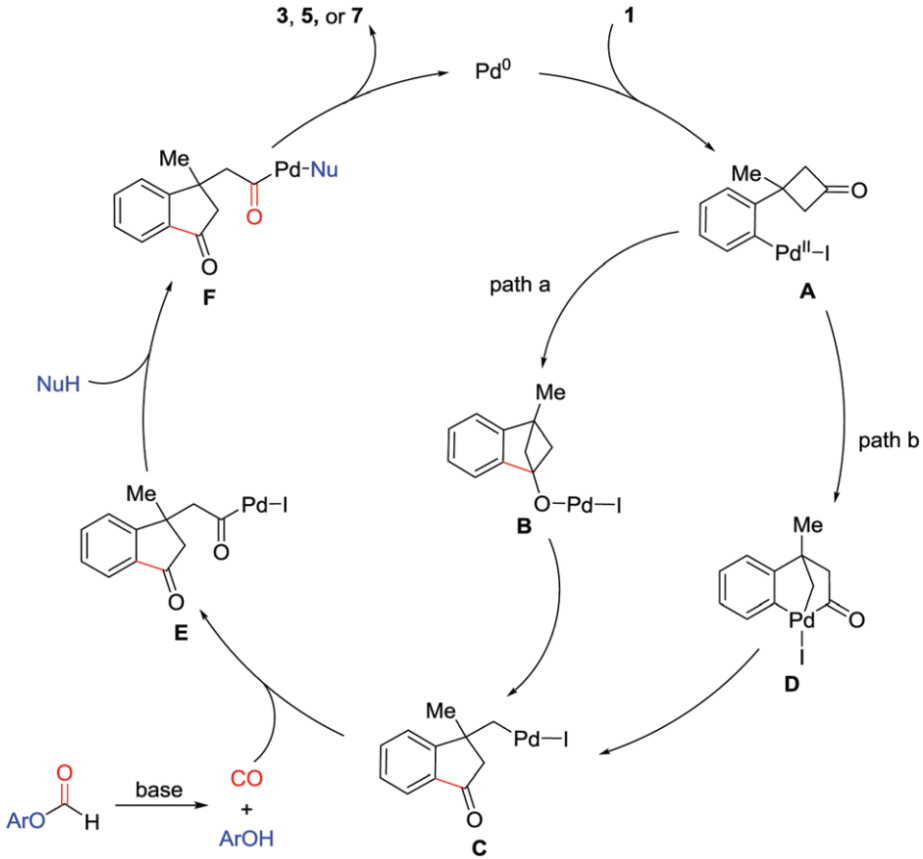




Dongbing Zhao; 10.1038/s41557-021-00746-7

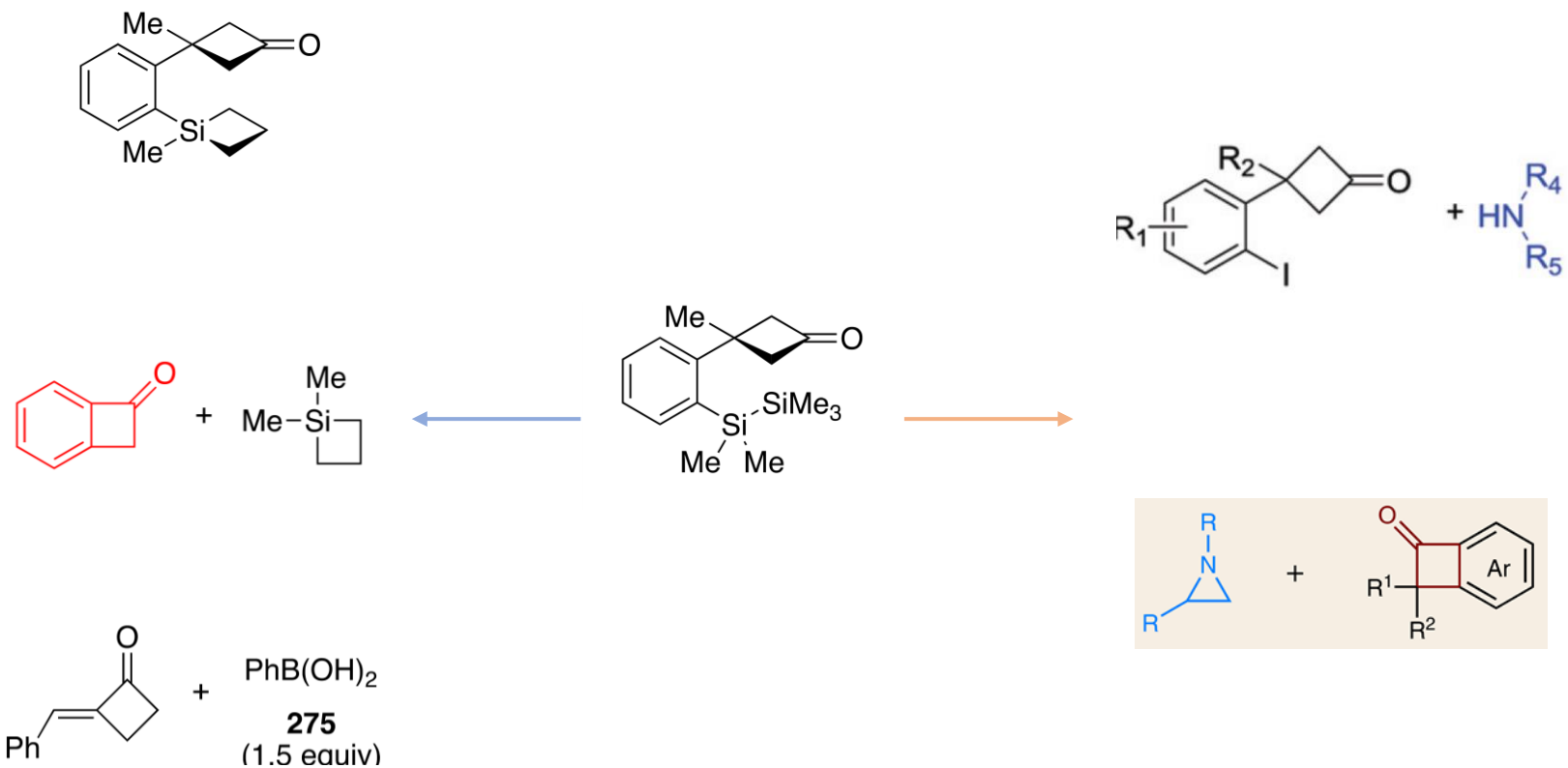
Palladium Catalysis





Li-Wen Xu.; *Org. Chem. Front.*, **2021**, *8,* 3398–3403.

Palladium Catalysis - summary

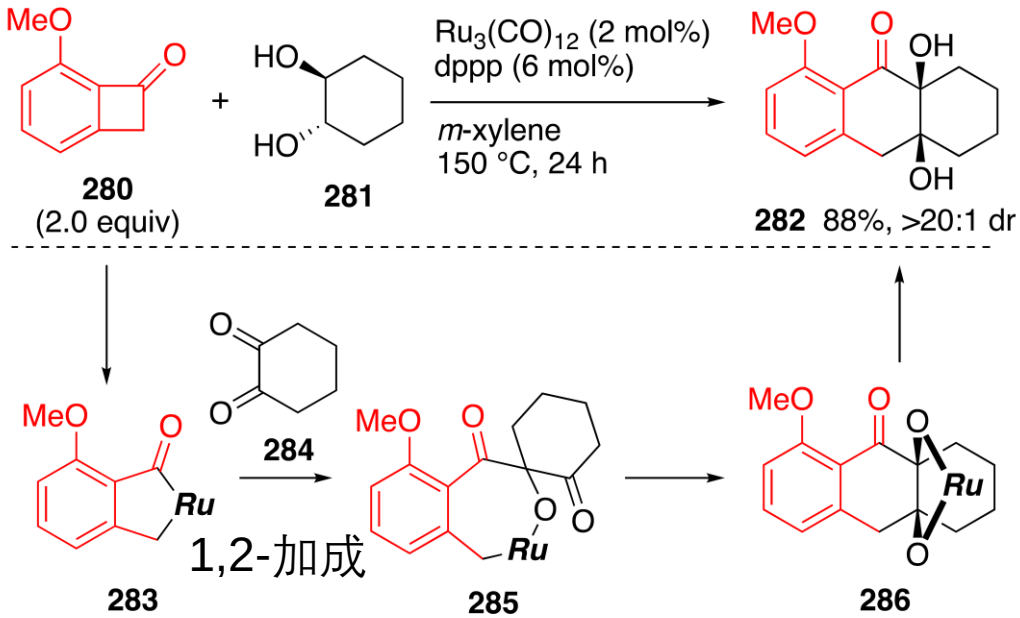


总结:

- 利用金属钯的优势，通过转金属或者其它方式实现反应类型的拓展

Contents

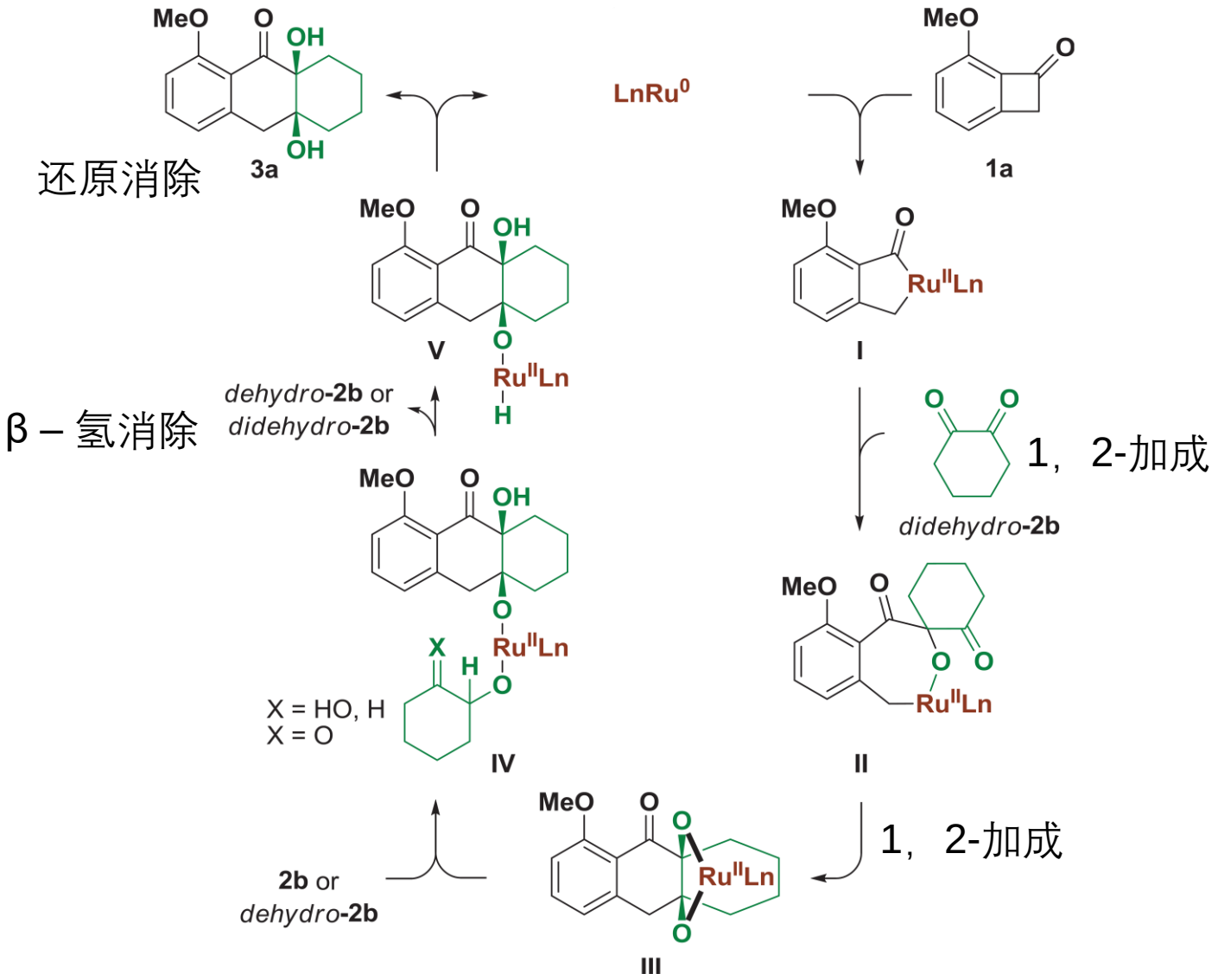
Ruthenium Catalysis



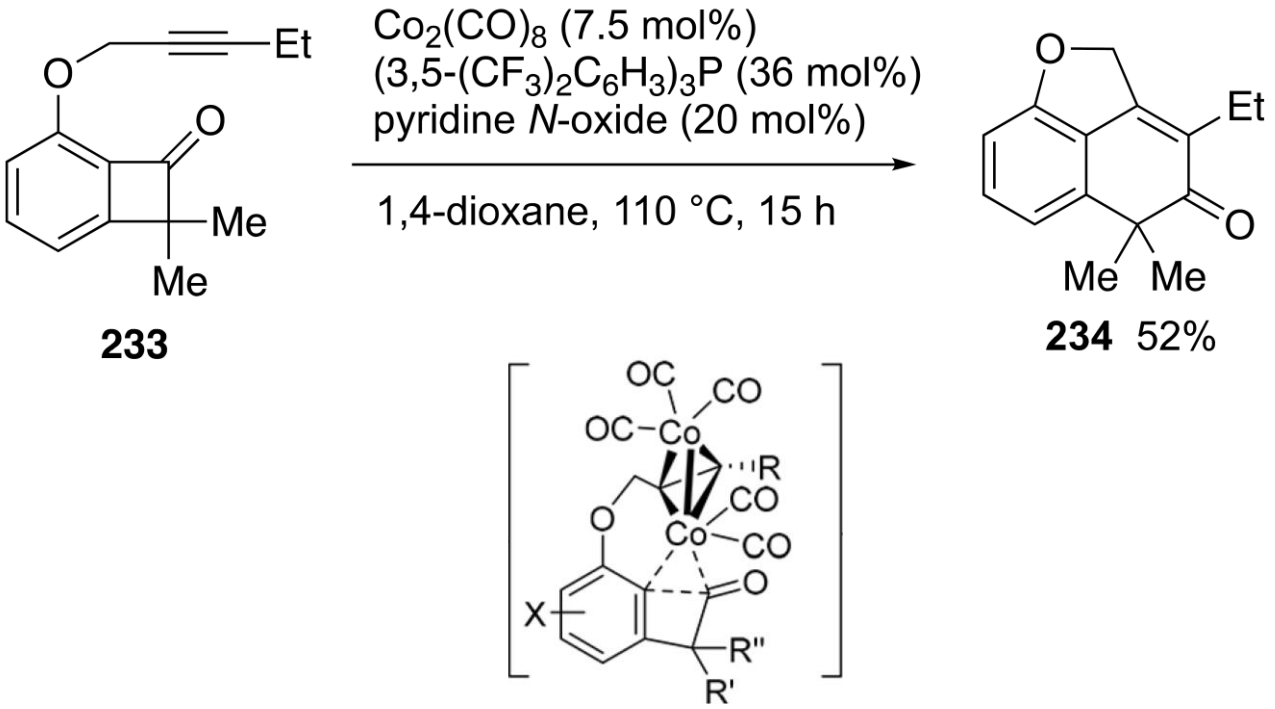
第一步怎么启动的?

Krische, M. *Science.* **2017**, *357*, 779−781.

Ruthenium Catalysis



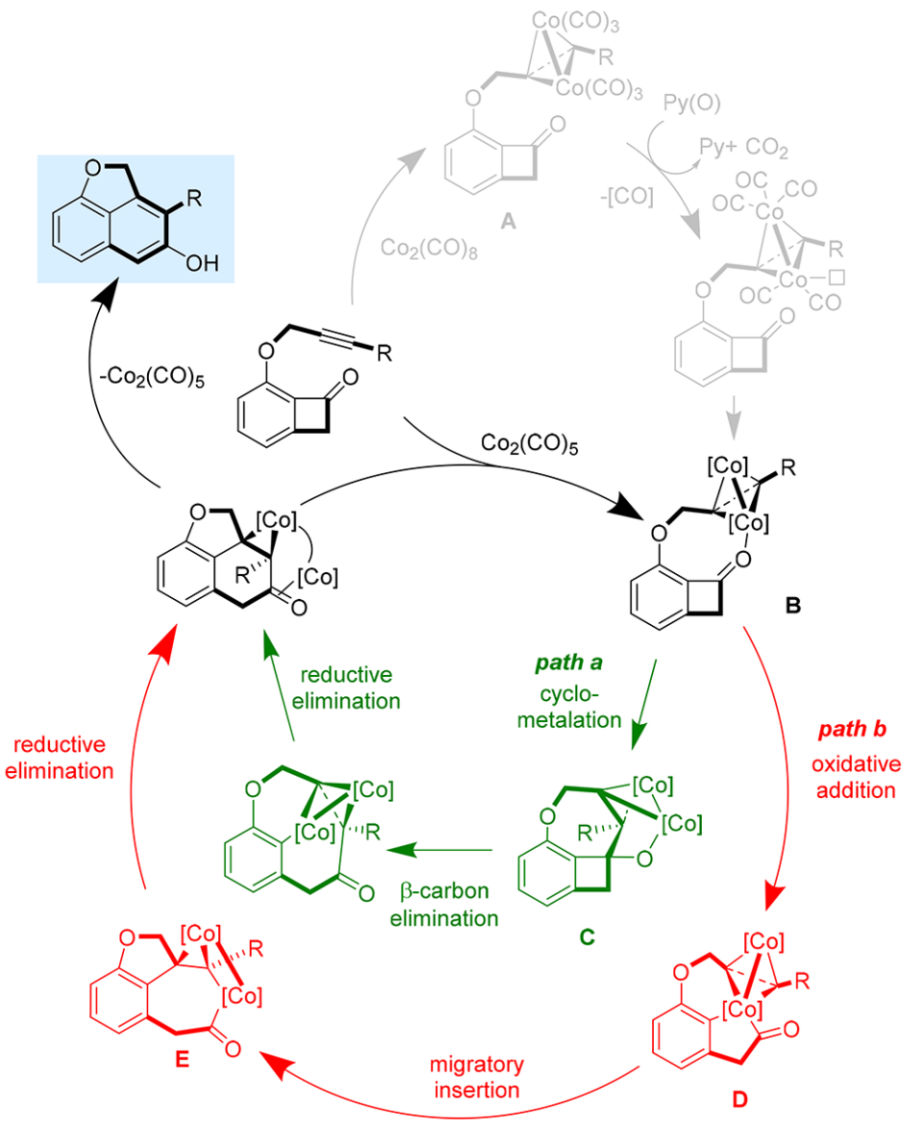
Cobalt Catalysis



首例钴催化酮的碳碳键活化

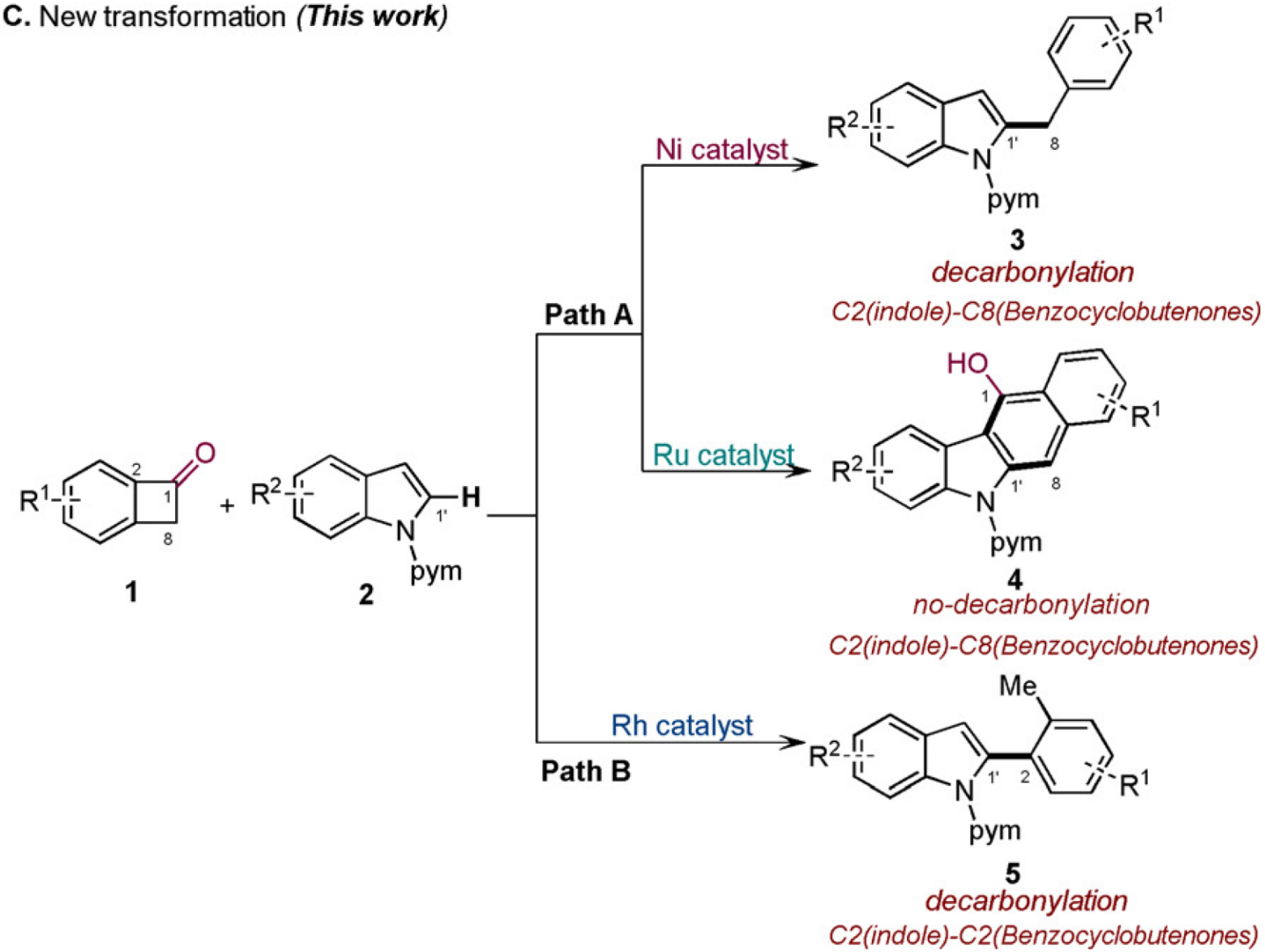
Dong, G; *ACS Catal*. **2018**, *8*, 845−849.

Cobalt Catalysis



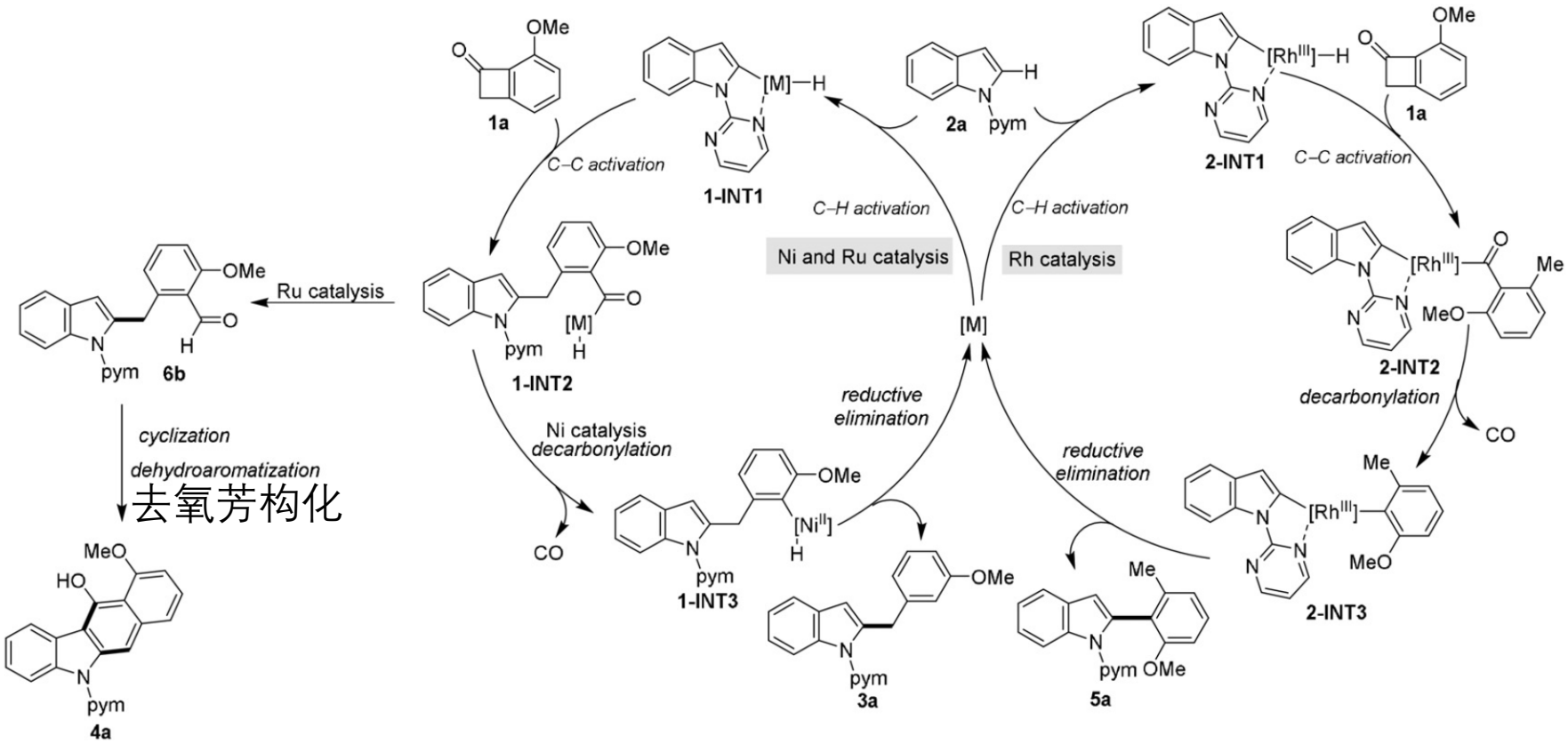
Nickel, Ruthenium, Rhodium Catalysis

C. New transformation ***(This work)***



Hao Wei.;*Angew. Chem. Int. Ed.* **2020**, *59*, 23537 –23543

Nickel, Ruthenium, Rhodium Catalysis



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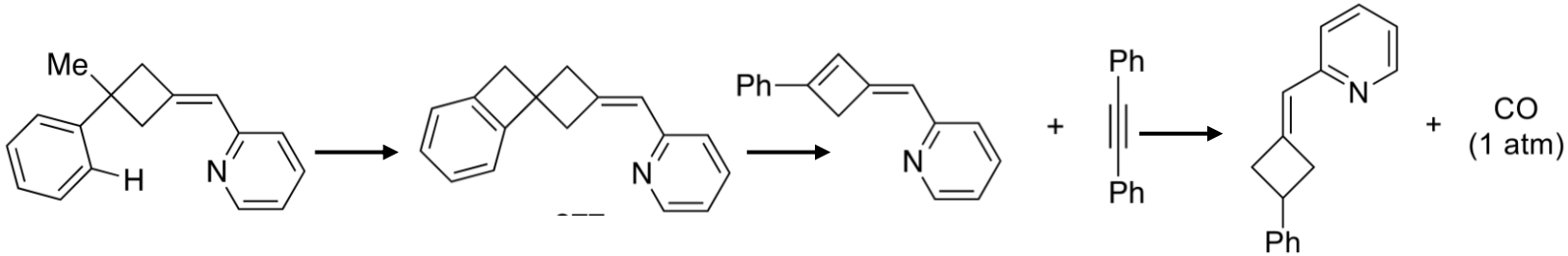
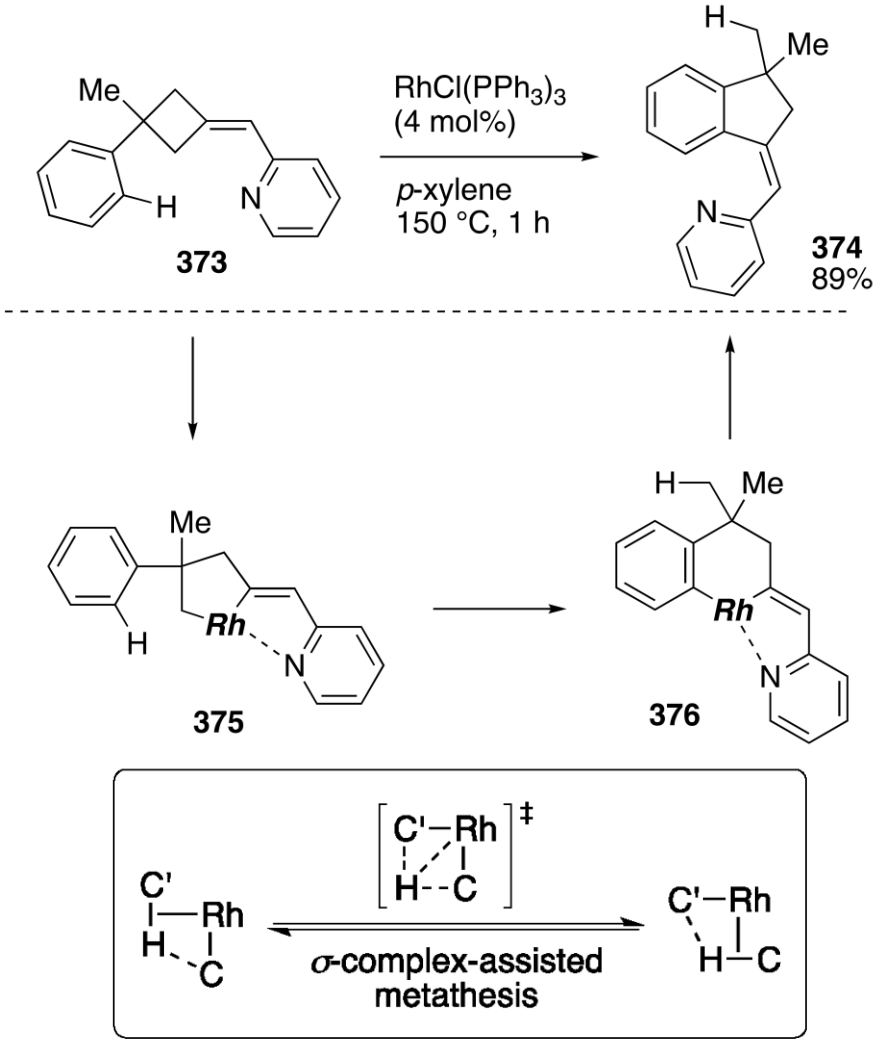
Alkylidenecyclobutanes - process



Alkylidenecyclobutanes

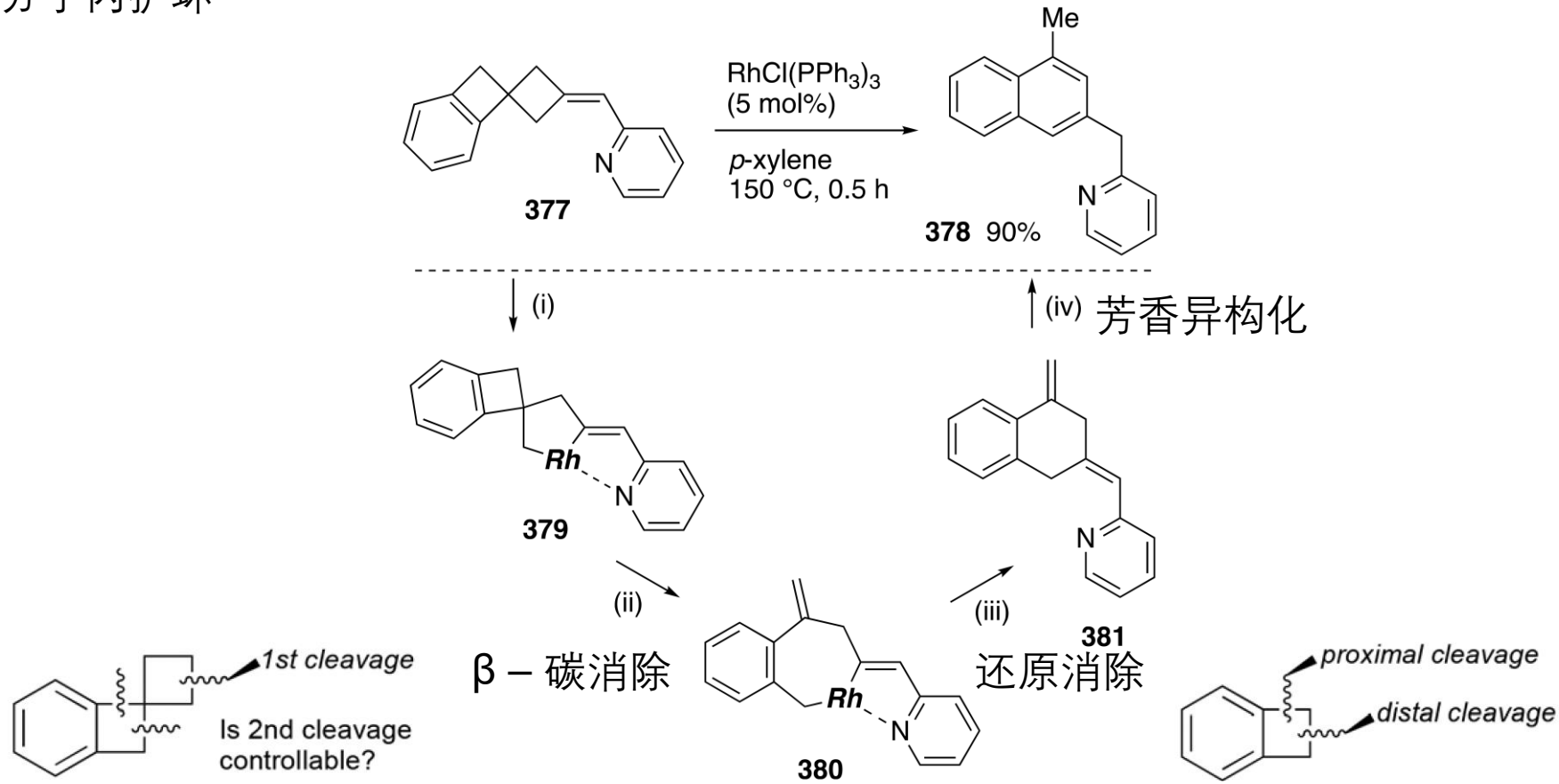
分子内碳氢键活化



Yuihara, I.; *Chem. Commun.* **2015**, *51*, 7393−7396.

Alkylidenecyclobutanes

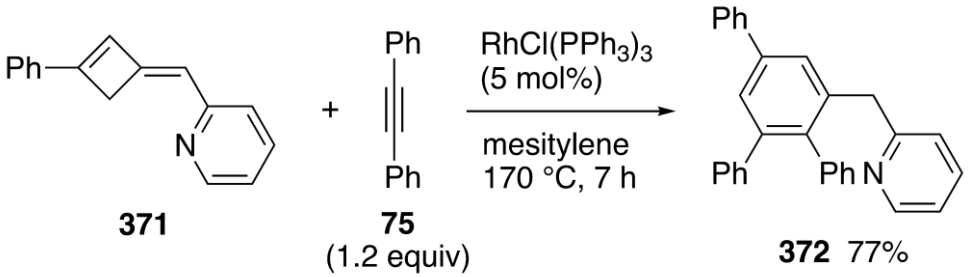
分子内扩环



Kondo, K.; *Org. Biomol. Chem*. **2016**, *14*, 7024−7027.

Alkylidenecyclobutanes

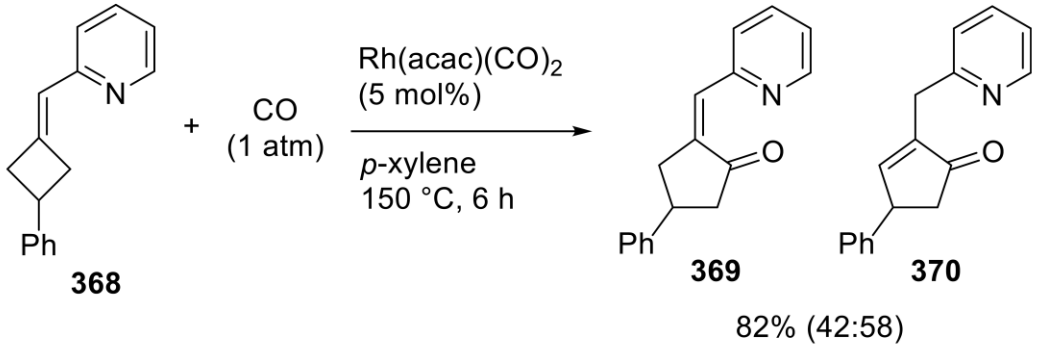
分子间插炔烃



Matsumoto, T.; *Org. Biomol. Chem.* **2016**, *14*, 5023−5027.

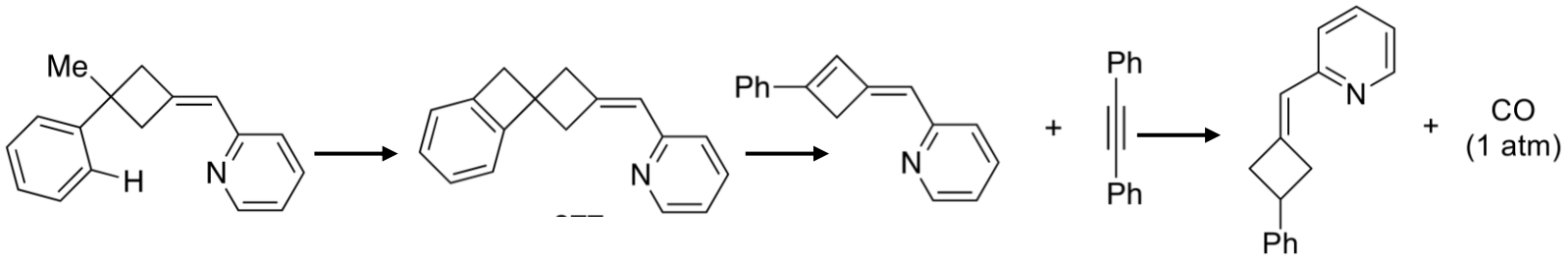
Alkylidenecyclobutanes

分子间插一氧化碳



Oyama, S.; *Chem. Lett*. **2017**, *46*, 1721−1723

Alkylidenecyclobutanes

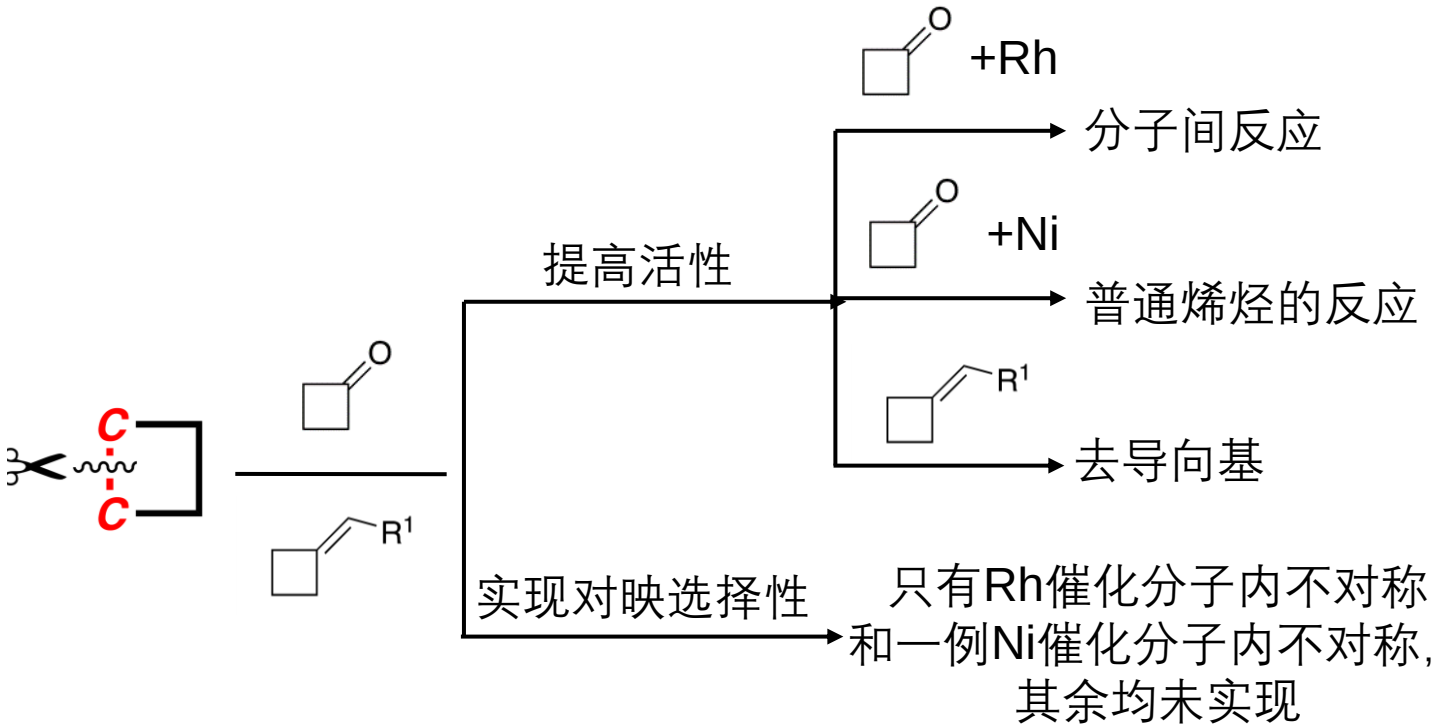


局限:

- 必须含有吡啶导向基，目前只有金属铑催化
- 没有实现烯烃及其不对称

Contents

Summary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C
O
R1
提高活性
O
+Rh
分子间反应
O
+Ni
普通烯烃的反应
R1
去导向基
实现对映选择性
只有Rh催化分子内不对称
和一例Ni催化分子内不对称,
其余均未实现