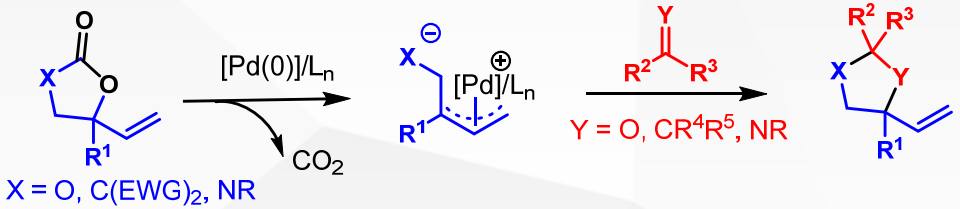
钯催化的脱羧[3+2]环加成反应



汇报人 ： 潘仁明
导师 ： 陆平 研究员
2022-06-10

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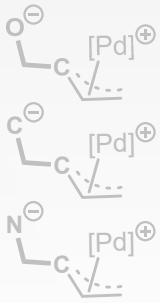
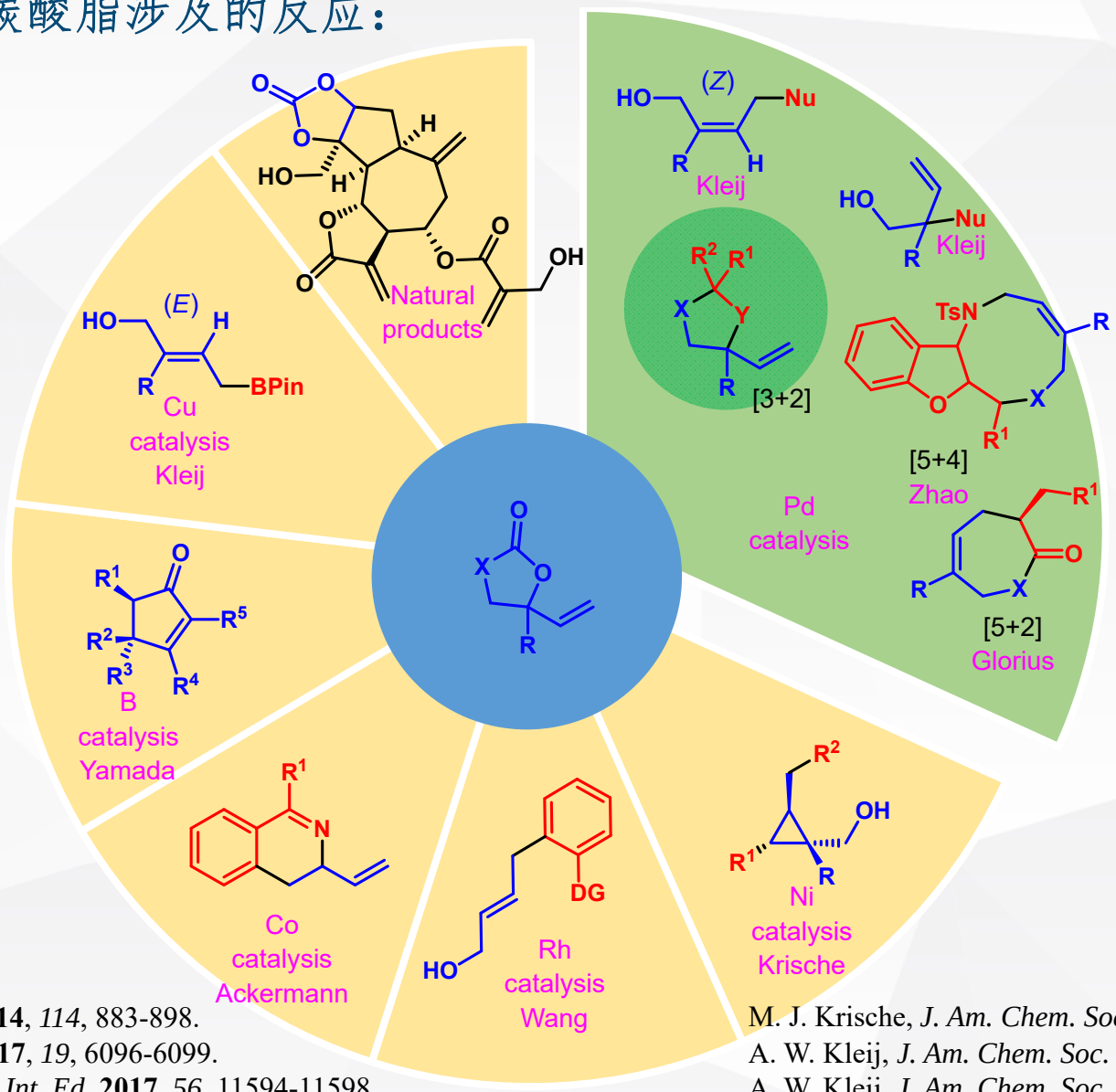


1. 背景

近年来乙烯基碳酸脂涉及的反应：

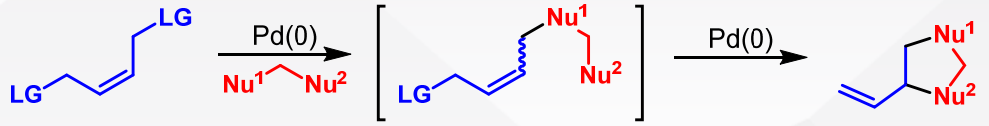


J. M. Yue, *Chem. Rev*. **2014**, *114*, 883-898.
A. W. Kleij, *Org. Lett.* **2017**, *19*, 6096-6099.
T. Yamada, *Angew.Chem. Int .Ed.* **2017**, *56*, 11594-11598.
Lutz Ackermann, *ACS Catal.* **2015**, *7*, 3430-3433.
H. Wang, *ACS Catal.* **2015**, *5*, 210-214.
M. J. Krische, *J. Am. Chem. Soc.* **2017**, *139*, 6847-6850.
A. W. Kleij, *J. Am. Chem. Soc.* **2016**, *138*, 11970-11978.
A. W. Kleij, *J. Am. Chem. Soc.* **2016**, *138*, 14194-14197.
Y. Zhao, *Angew.Chem. Int .Ed.* **2017**, *56*, 2927-2931.
F. Glorius, *J. Am. Chem. Soc.* **2018**, *140*, 3551-3554.

1. 背景

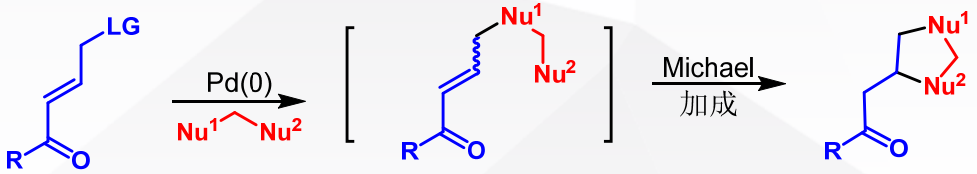
钯催化生成偶极子方式：

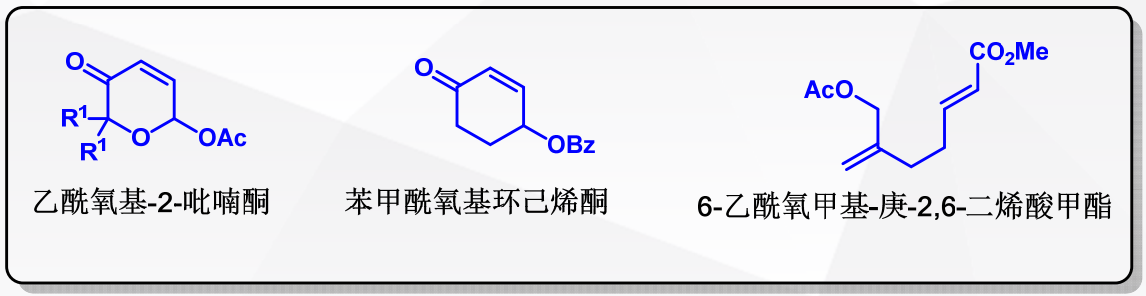
1) 双烯丙基体系生成的偶极子:



J. Tsuji, *Tetrahedron Lett*. **1965**, *49*, 4387-4388. B. Trost, *J. Am. Chem. Soc*. **1973**, *95*, 292-294. B. Trost, *Acc. Chem. Res*. **1980**, *13*, 385-393.

2) 带有烯丙基离去基团的Michael受体生成的偶极子:



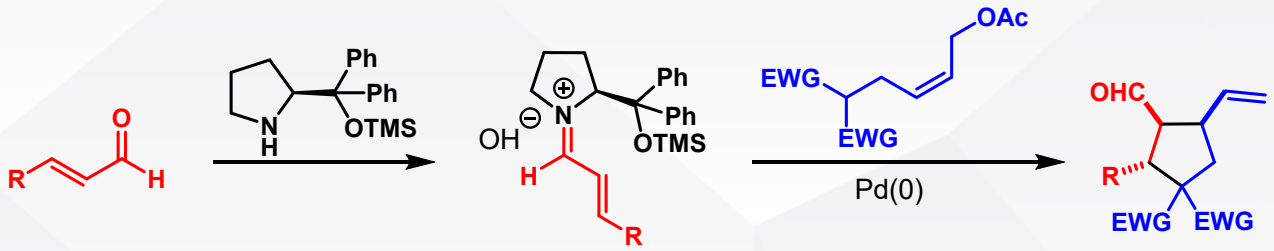


B. Trost, *Chem Rev*. **2003**, *103*, 2921-2944. C. Jousse, *Eur. J. Org. Chem*. **2001**, *2001*, 3631-3640. J. Yu, *Org, Chem. Front*. **2016**, *3*, 714-719.

1. 背景

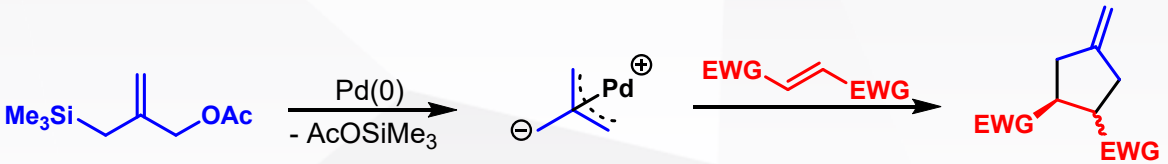
钯催化的[3+2]环加成反应：

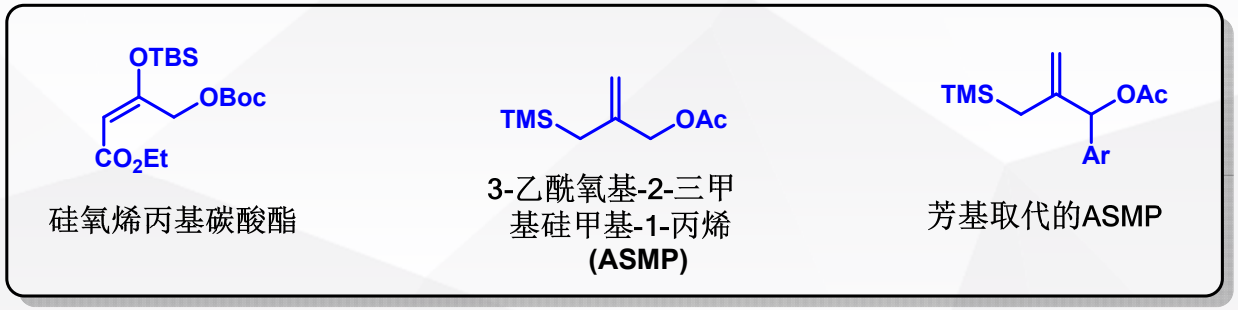
3) 有机催化剂生成的亲偶极子:



B. Trost, *J. Am. Chem. Soc*. **1979**, *101*, 6429-6432. K. A. Jøgensen, *Angew. Chem. Int. Ed.* **1986**, *25*, 1-20.
Y. Hayashi, *Angew. Chem. Int. Ed.* **2005**, *44*, 4212-4215. A. Córdova, *Angew. Chem. Int. Ed.* **2013**, *52*, 6050-6054.

4) 3-乙酰氧基-2-三甲基硅甲基-1-丙烯生成的偶极子：



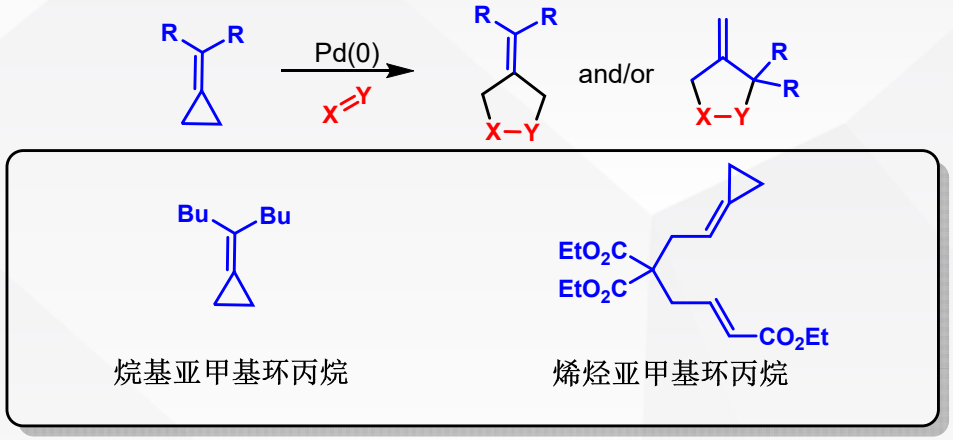


M. Lautens, *Chem. Rev.* **1996**, *96*, 49-92. B. Trost, *Pure. Appl. Chem.* **1988**, *60*, 1615-1626.;
S. Yamago, *Org. React.* **2003**, *61*, 1-217. I. Kumar, *RSC Adv.* **2014**, *4*, 16397-16408.

1. 背景

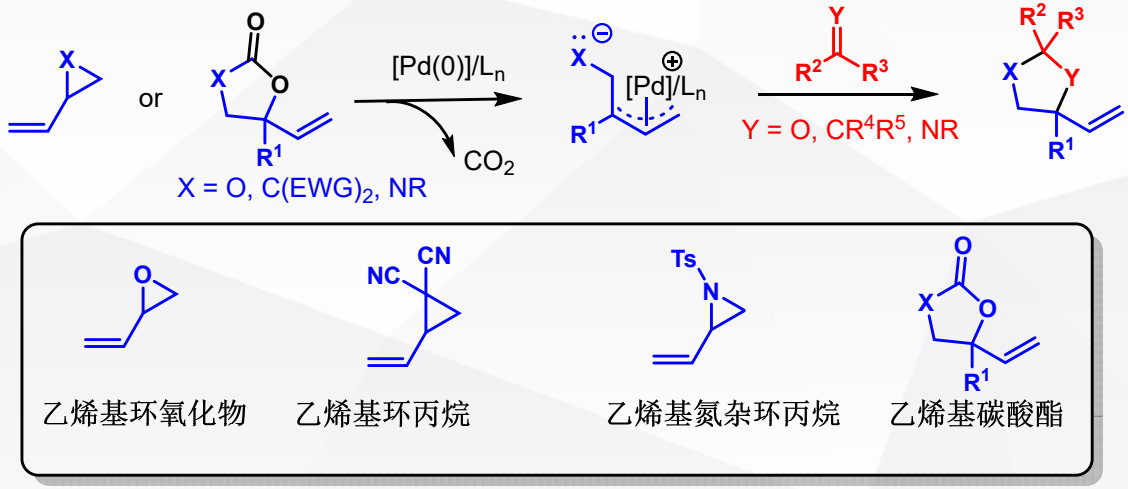
钯催化的[3+2]环加成反应：

5) 烯基环丙烷类作为异偶极子:



P. Binger, *Angew. Chem. Int. Ed.* **1982**, *21*, 622-623. Y. Yamamoto, *Angew. Chem. Int. Ed.* **2001**, *40*, 1298-1230.

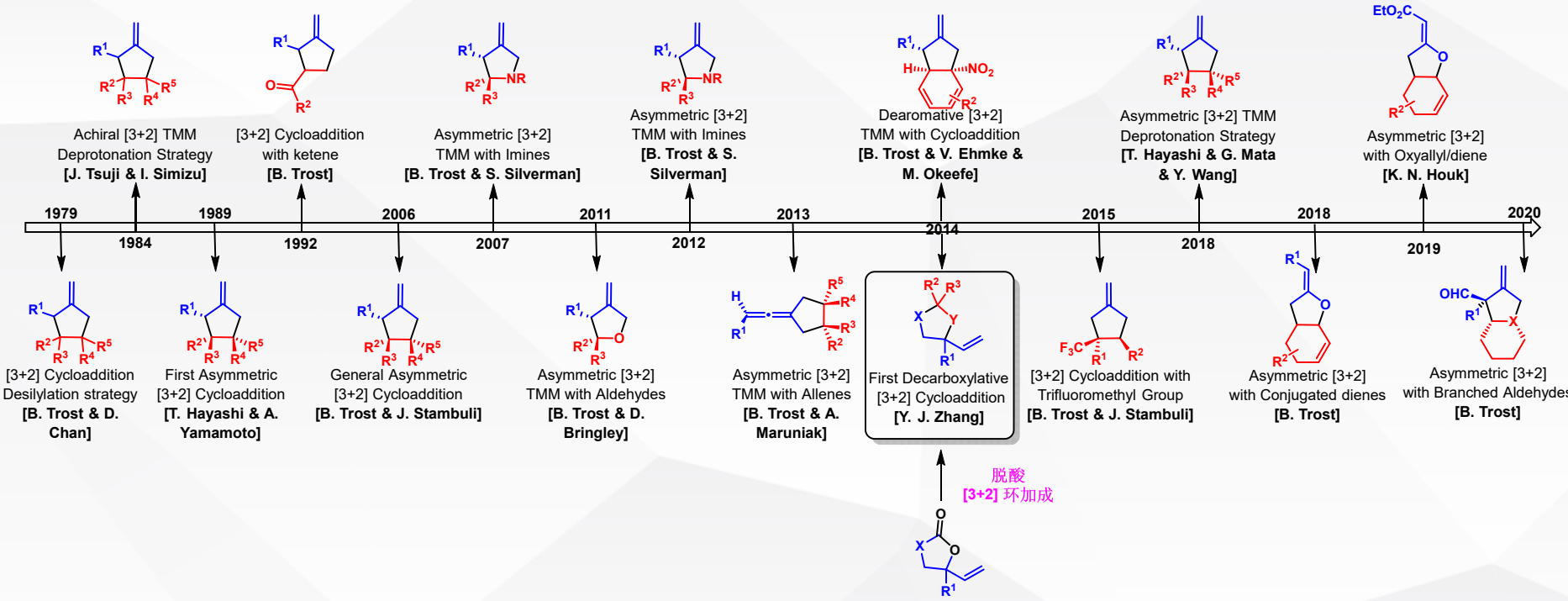
6) 乙烯基环杂丙烷或乙烯基环碳酸脂类作为异偶极子:



J. Tsuji, *Tetrahedron Lett.* **1985**, *26*, 3825-3828. M. Suzuki, *Macromolecules.* **1989**, *22*, 1505-1507.
M. Suzuki, *Macromolecules*, **1993**, *26*, 4748-4750. Y. J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 6439-6442.

1. 背景

四十年来钯催化的[3+2]环加成反应：

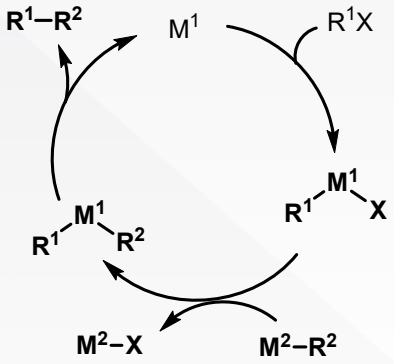


B. Trost, *J. Am. Chem. Soc.* **1979**, *101*, 6432-6433. J. Tsuji, *Tetrahedron Lett.* **1984**, *25*, 5183-5186.
J. Tsuji, *Tetrahedron Lett.* **1985**, *26*, 3825-3828. B. Trost, *J. Am. Chem. Soc.* **1989**, *111*, 6482-6484.
B. Trost, *J. Am. Chem. Soc.* **1992**, *114*, 7903-7904. B. Trost, *J. Am. Chem. Soc.* **2006**, *128*, 13328-13329.
B. Trost, *J. Am. Chem. Soc.* **2007**, *129*, 12398-12399. B. Trost, *J. Am. Chem. Soc.* **2011**, *133*, 19483-19497.
B. Trost, *J. Am. Chem. Soc.* **2012**, *134*, 4941-4954. B. Trost, *Angew. Chem., Int. Ed.* **2013**, *52*, 6262-6264.
B. Trost, *Org. Lett.* **2014**, *16*, 2708-2710. Y. J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 6439-6442. B. Trost, *Org. Lett.* **2018**, *20*, 39388-3940.
K. N. Houk, *J. Am. Chem. Soc.* **2019**, *141*, 12382-12387. G. Poli, *Eur. J. Inorg. Chem.* **2020**, *20*, 942-961.
B. Trost, *Narure Chemistry*, **2020**, *12*, 294-301. B. Trost, *Acc. Chem. Res.* **2020**, *53*, 1293-1305.

1. 背景

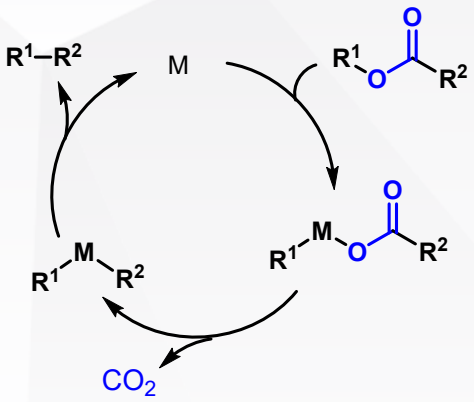
常见交叉偶联与脱羧偶联对比：

常见交叉偶联：



versus

脱羧交叉偶联：



优势：

- 羧酸衍生物是普遍存在的廉价易得反应物；
- 中性条件下，脱羧可以促进反应中间体的形成；
- 唯一的化学计量副产品是CO_2；
- ……

M. Taherimehr, *Catal. Sci. Technol.* **2012**, *2*, 2169-2187. C. Young, *Green Chem.* **2010**, *12*, 1514-1539.
A. W. Kleij, *Angew. Chem., Int. Ed.* **2010**, *49*, 9822-9837. J. A. Tunge, *Chem. Rev.* **2011**, *111*, 1846-1913.

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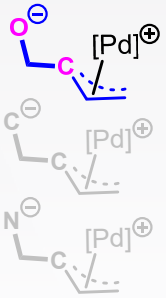
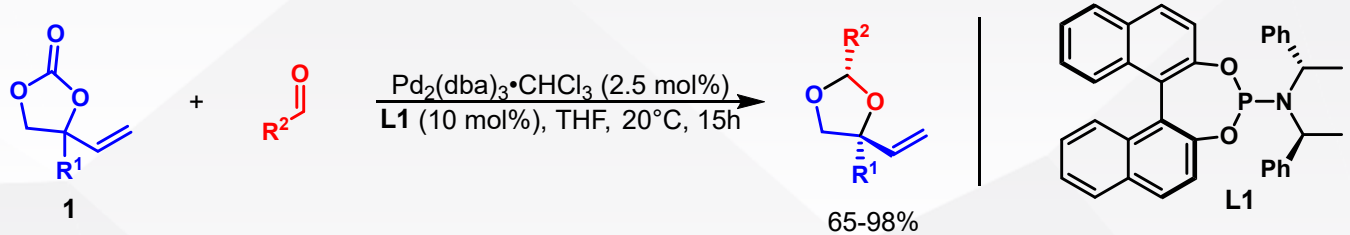
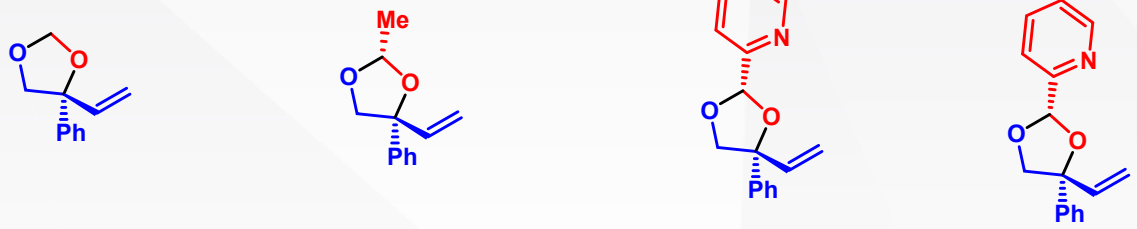
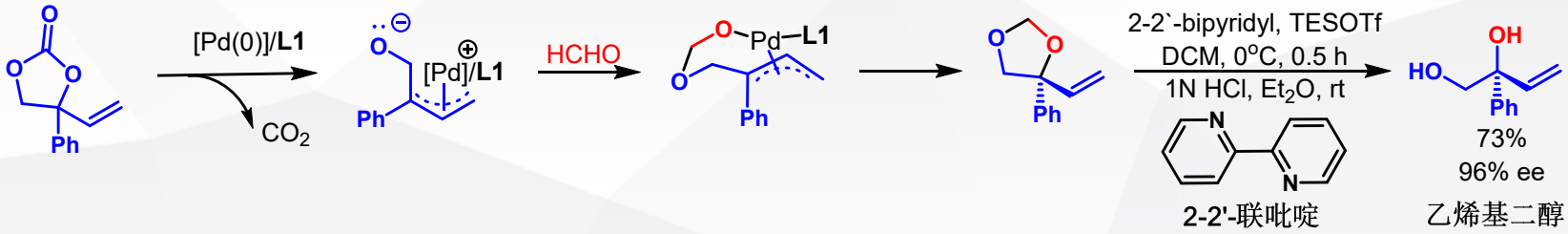


2.1 *C,O*-偶极子

首次脱羧[3+2]环加成：

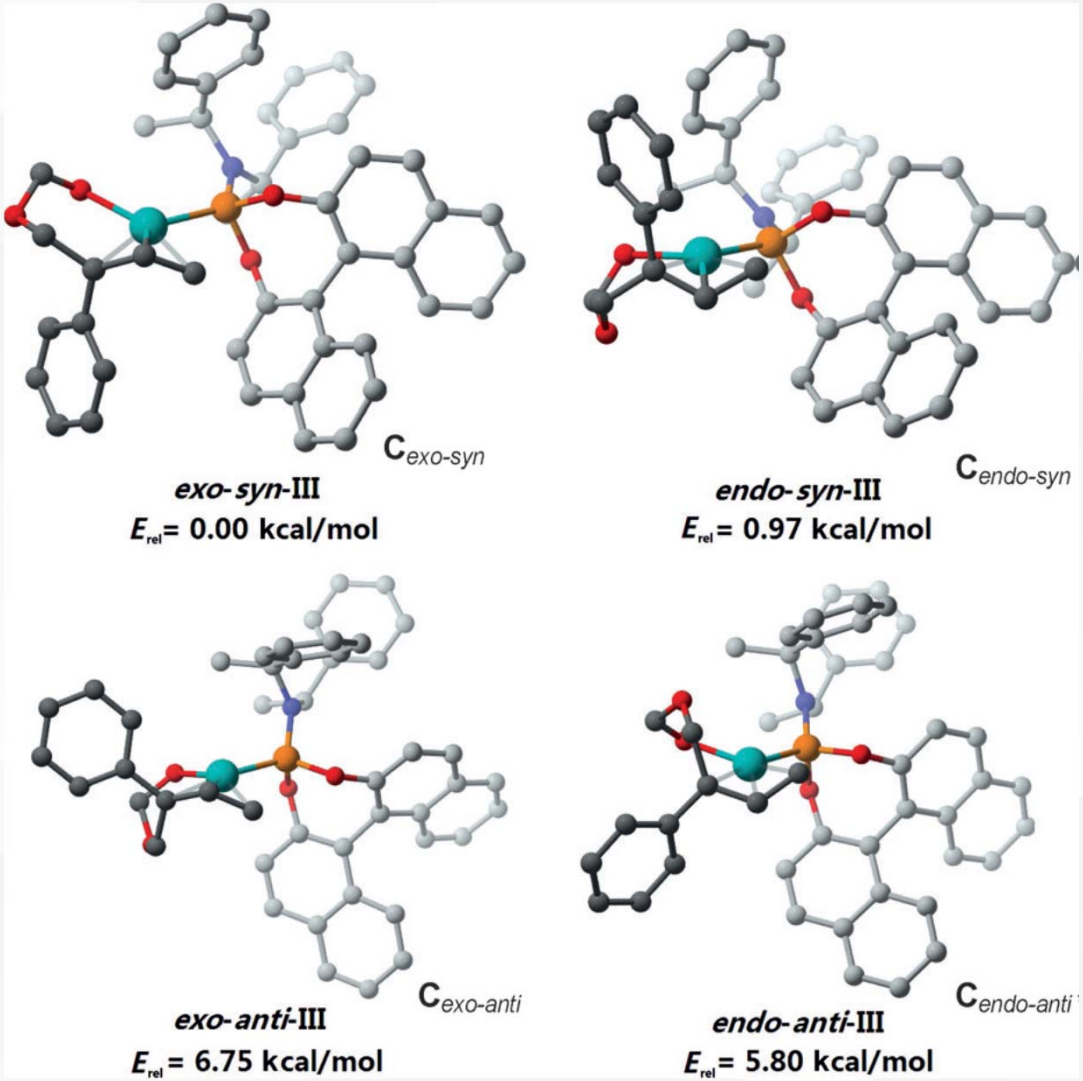






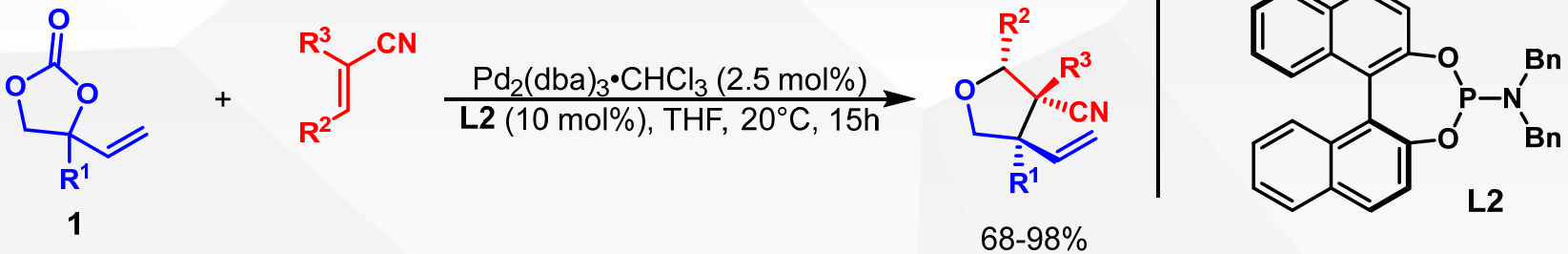
2.1 *C,O*-偶极子

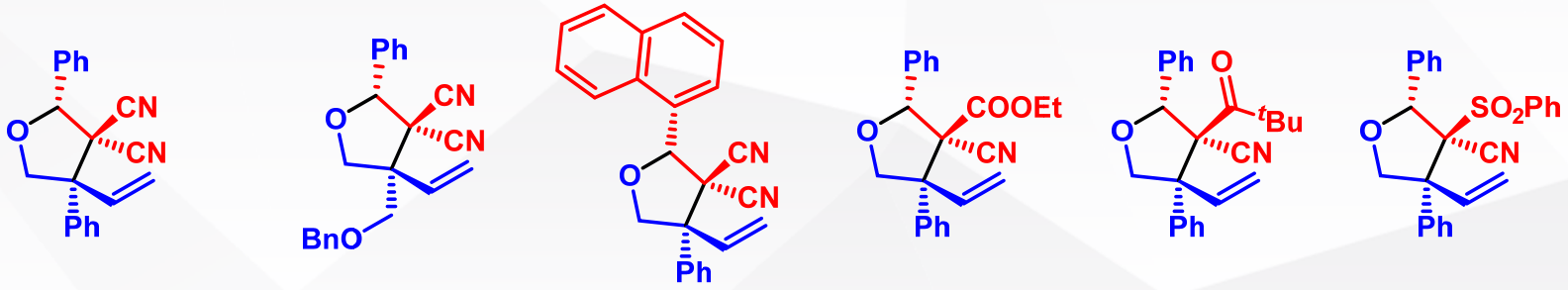
钯中间体的四种可能异构体的计算结构及其相对能量：



2.1 *C,O*-偶极子

相邻季碳立体中心的构建：





98%
14:1 dr
94% ee

68%
4:1 dr
83% ee

95%
19:1 dr
92% ee

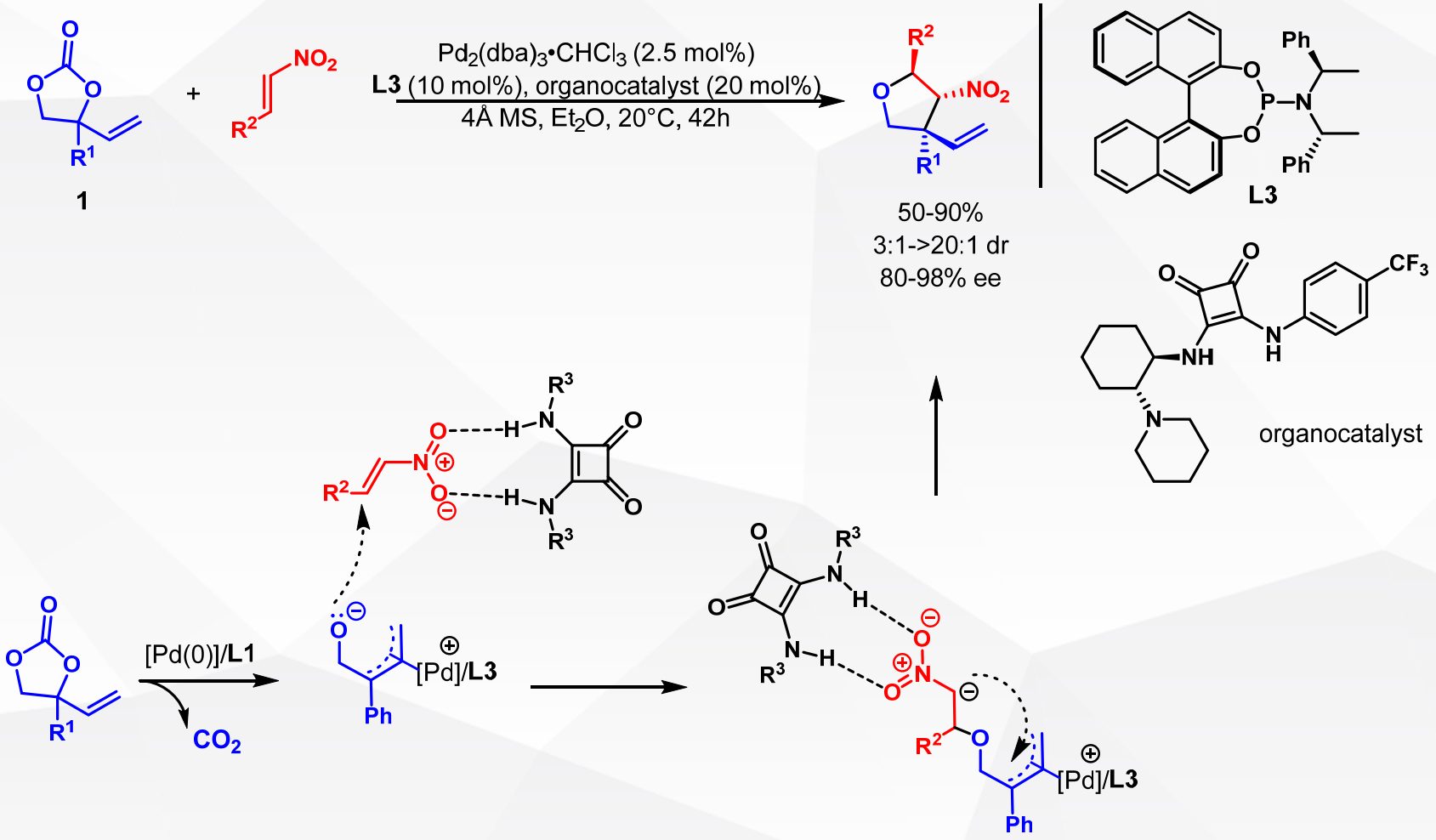
98%
8:1 dr
80% ee

93%
11:1 dr
93% ee

94%
7:1 dr
98% ee

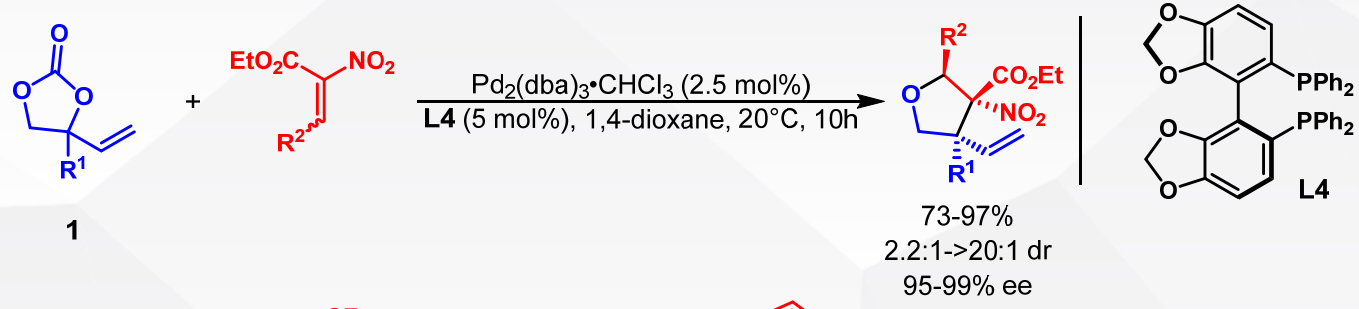
2.1 *C,O*-偶极子

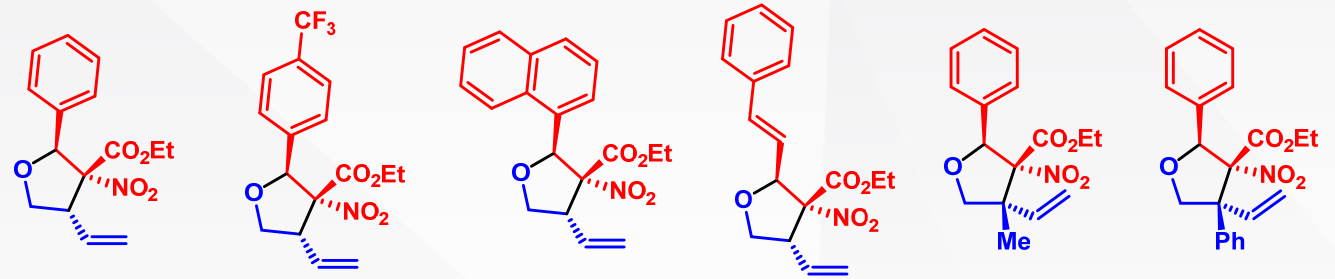
钯络合物与方酰胺的协同催化作用：

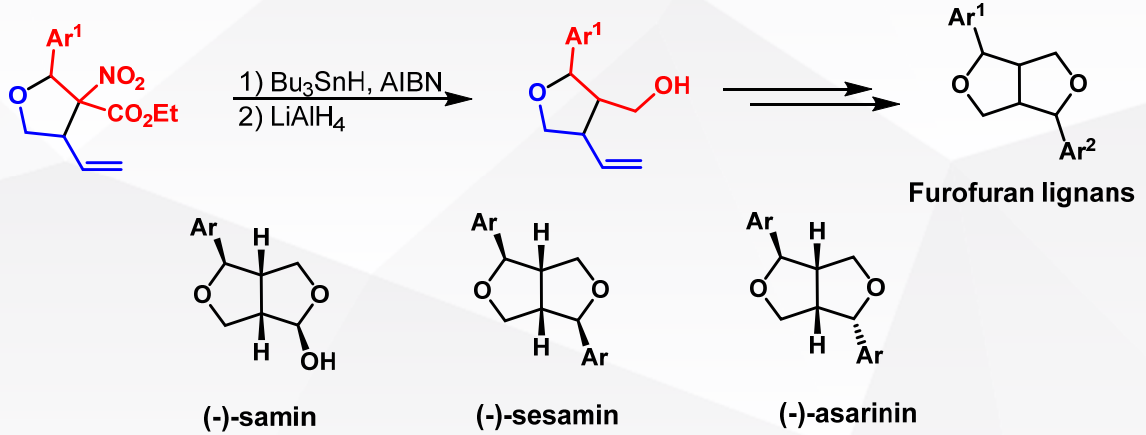


2.1 *C,O*-偶极子

三个连续立体中心的四氢呋喃类化合物的构建:

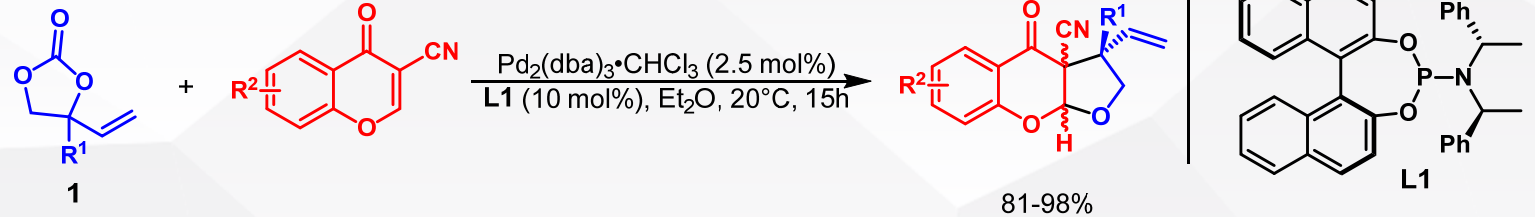


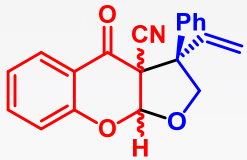


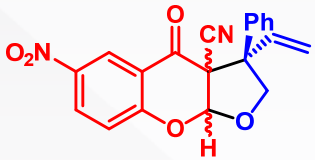


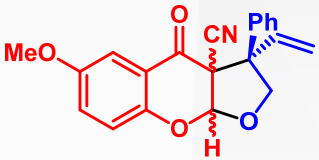
2.1 *C,O*-偶极子

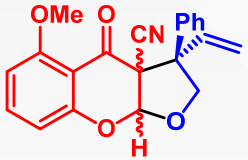
相邻季碳立体中心的呋喃二氢吡喃类化合物的构建：

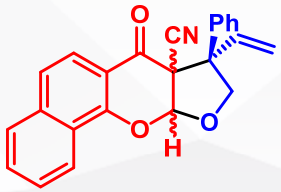


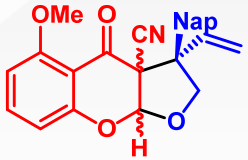

98%, 2.1:1 dr
96% ee, 94% ee

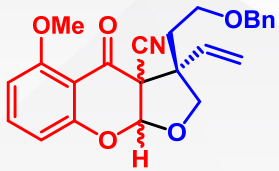

92%, 1:1 dr
78% ee, 61% ee

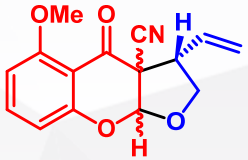

90%, 3.8:1 dr
96% ee, 91% ee


92%, 4.2:1 dr
97% ee, 95% ee


92%, 3.9:1 dr
95% ee, 90% ee

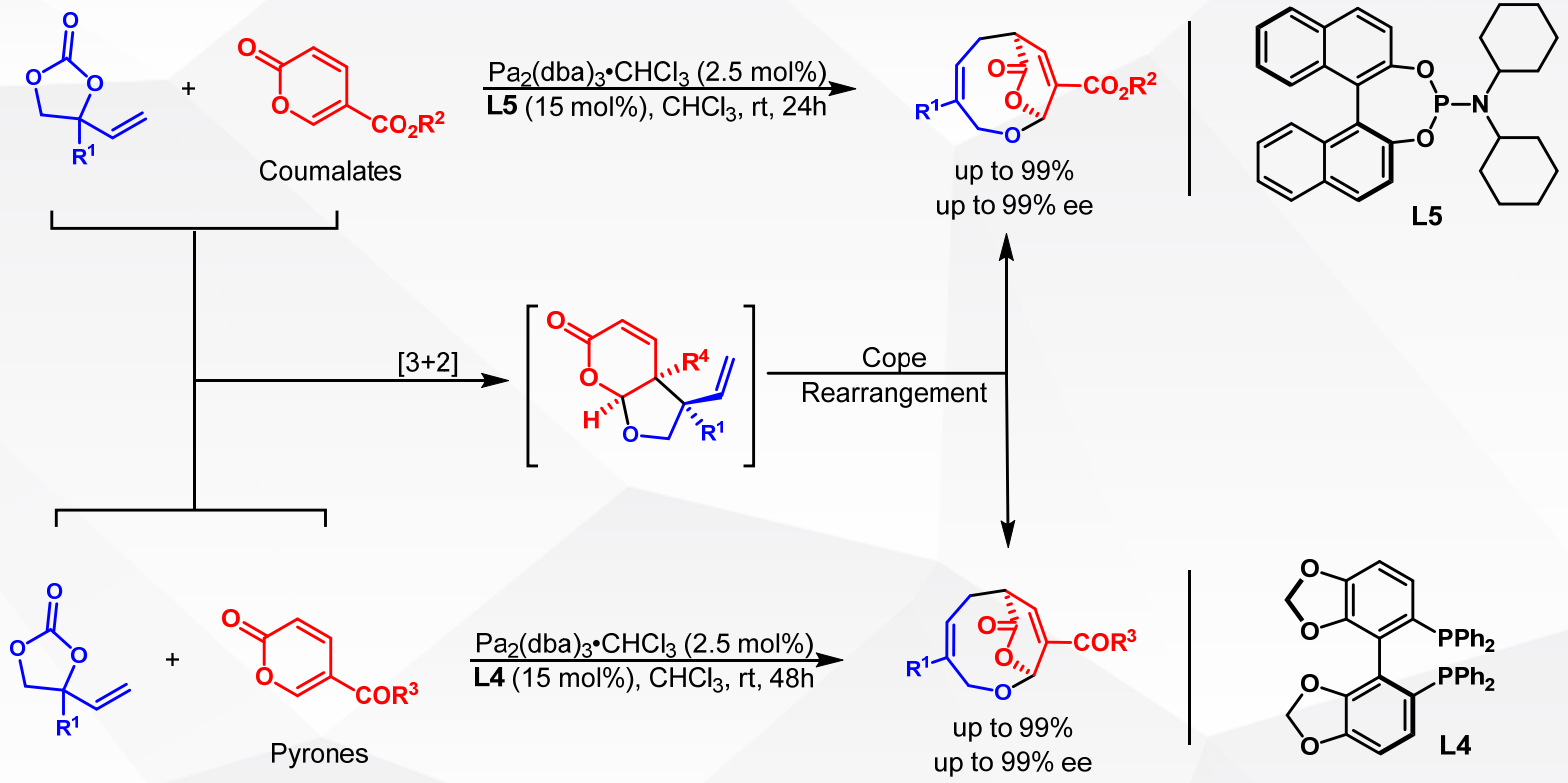

88%, 4.0:1 dr
88% ee, 80% ee


88%, 3.4:1 dr
94% ee, 87% ee


96%, 7.5:1 dr
95% ee, 95% ee

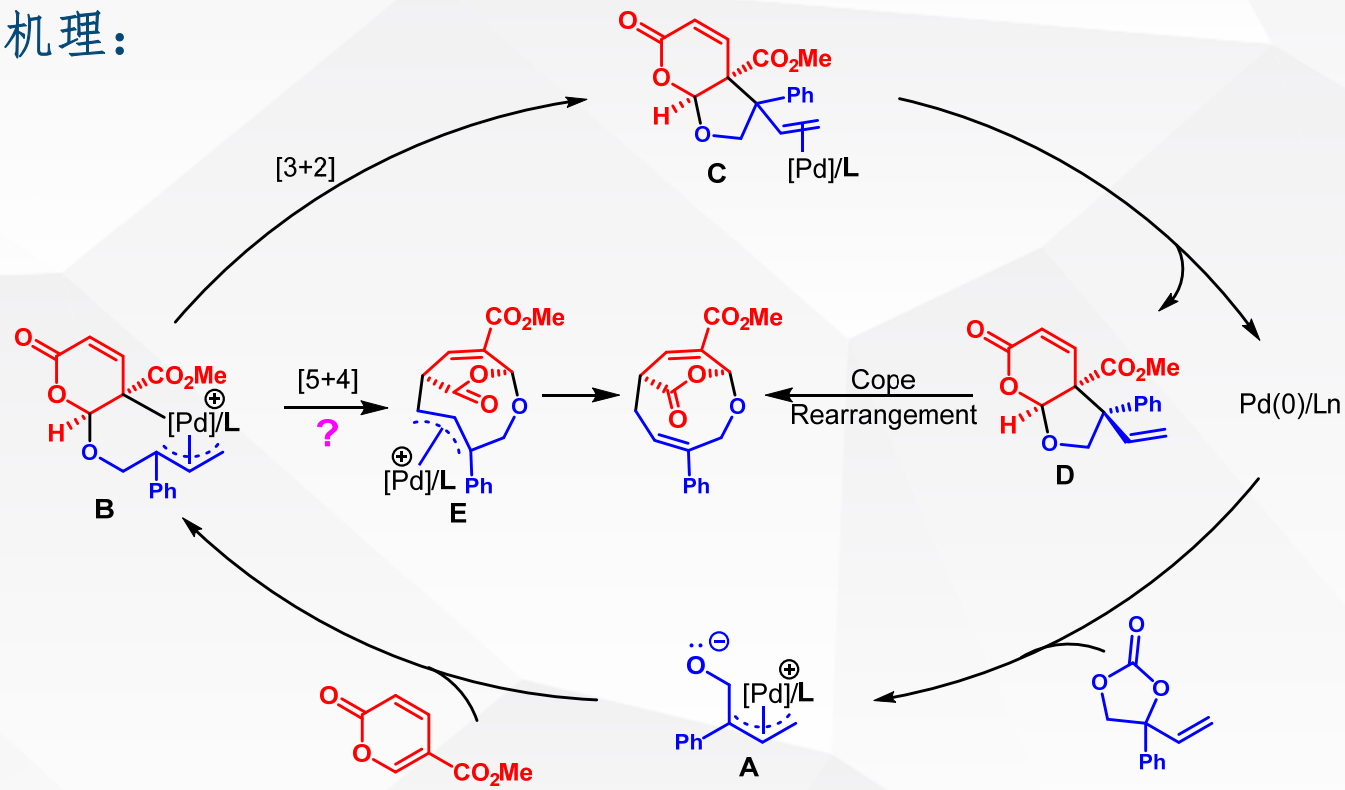
2.1 *C,O*-偶极子

串联环加成和Cope重排：



2.1 *C,O*-偶极子

可能的机理：



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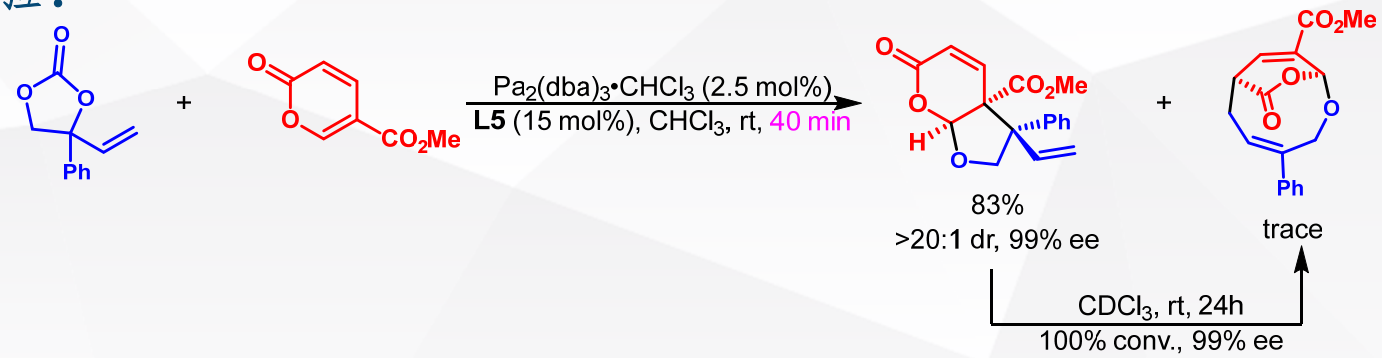
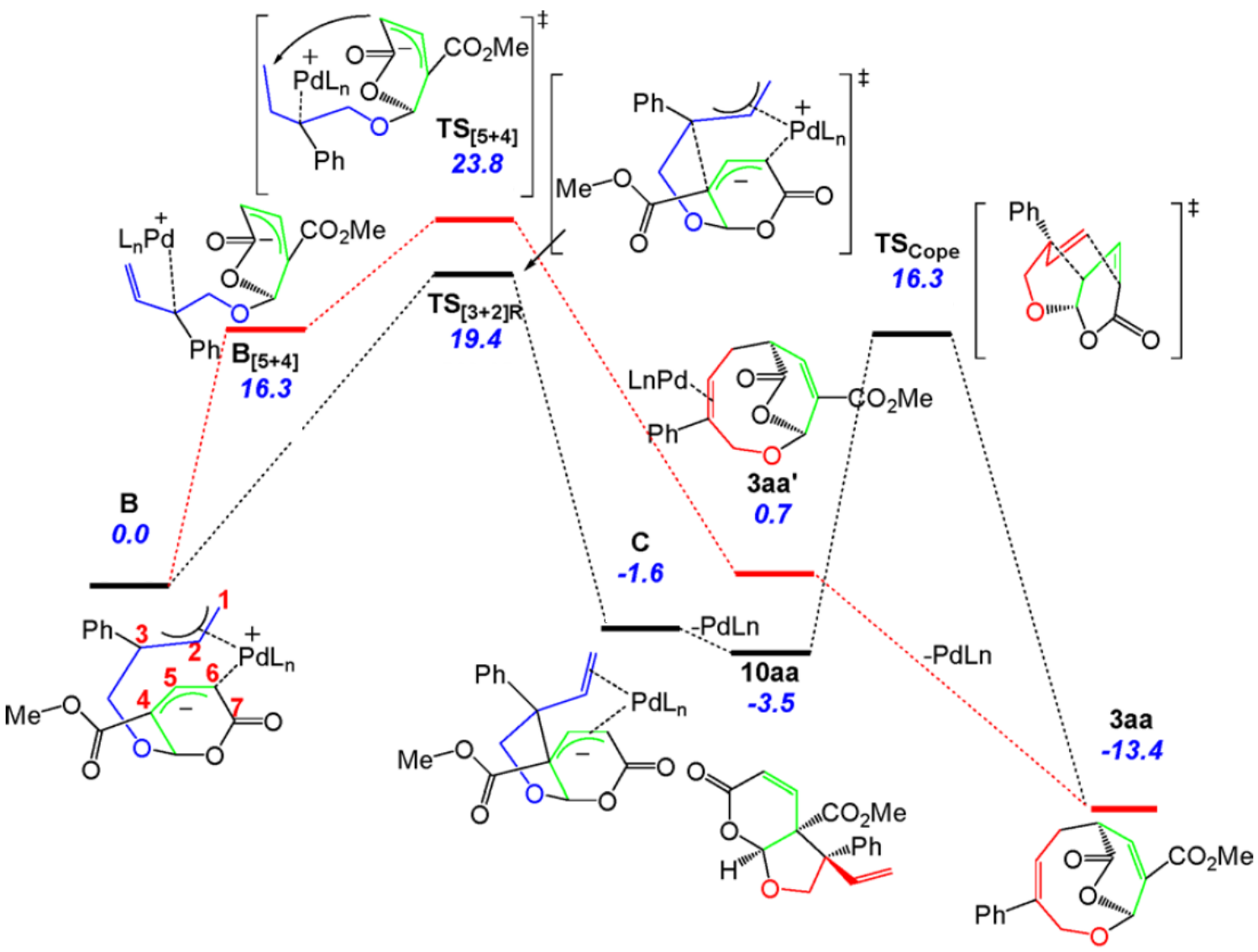


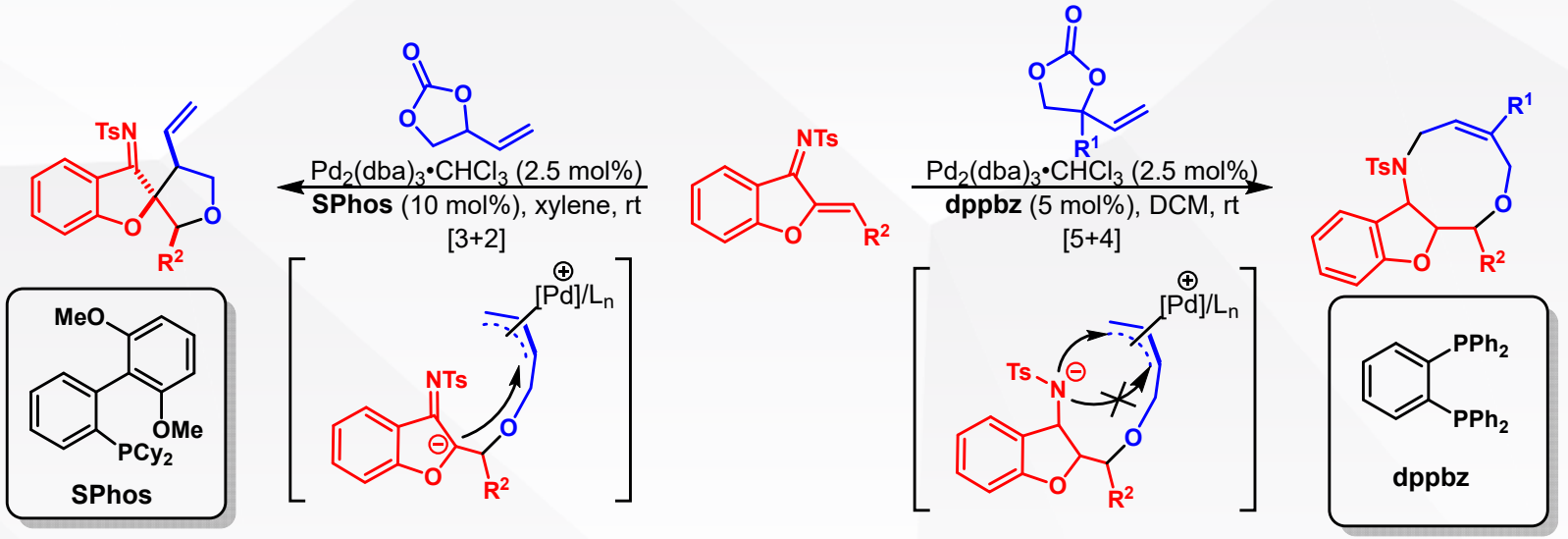
2.1 *C,O*-偶极子

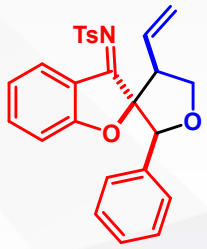
吉布斯自由能曲线：



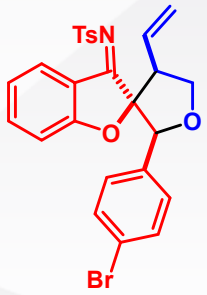
2.1 *C,O*-偶极子

对甲苯磺酰基氮杂二烯[3+2]环加成：

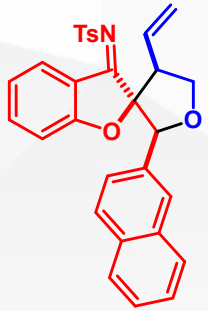




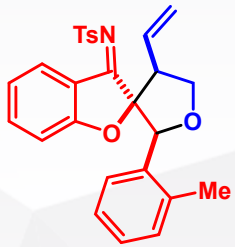
75%, 12:1 dr



76%, 19:1 dr



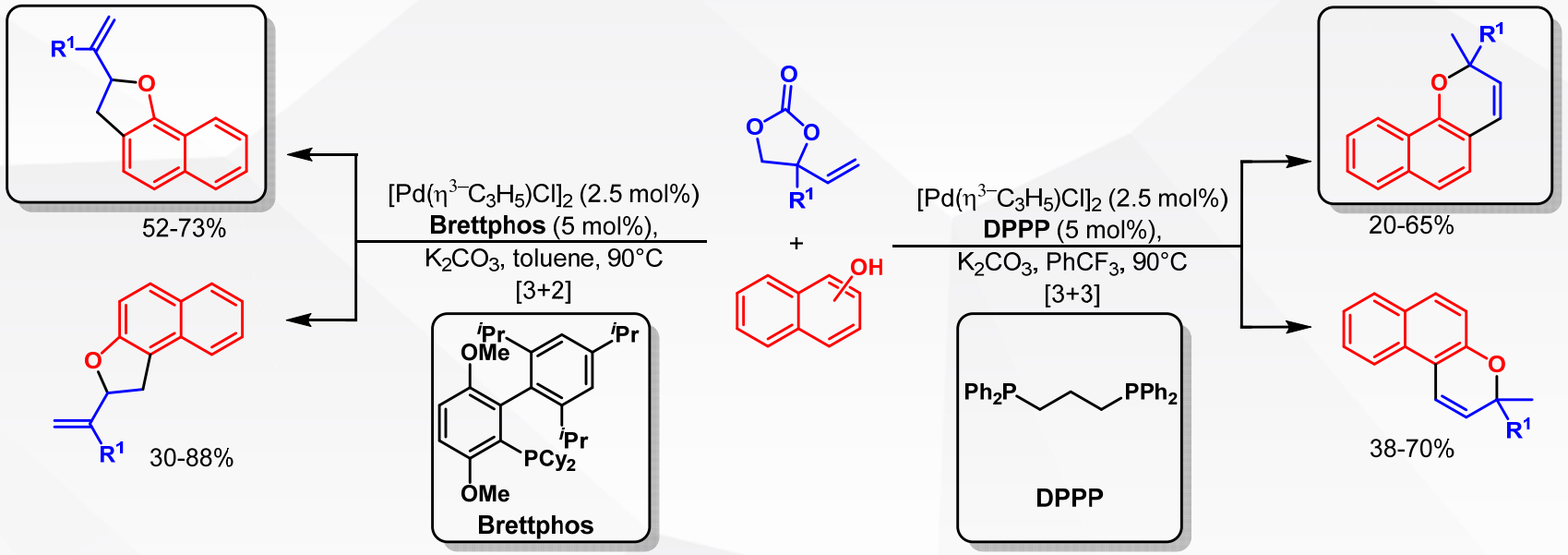
51%, 8:1 dr



75%, 12:1 dr

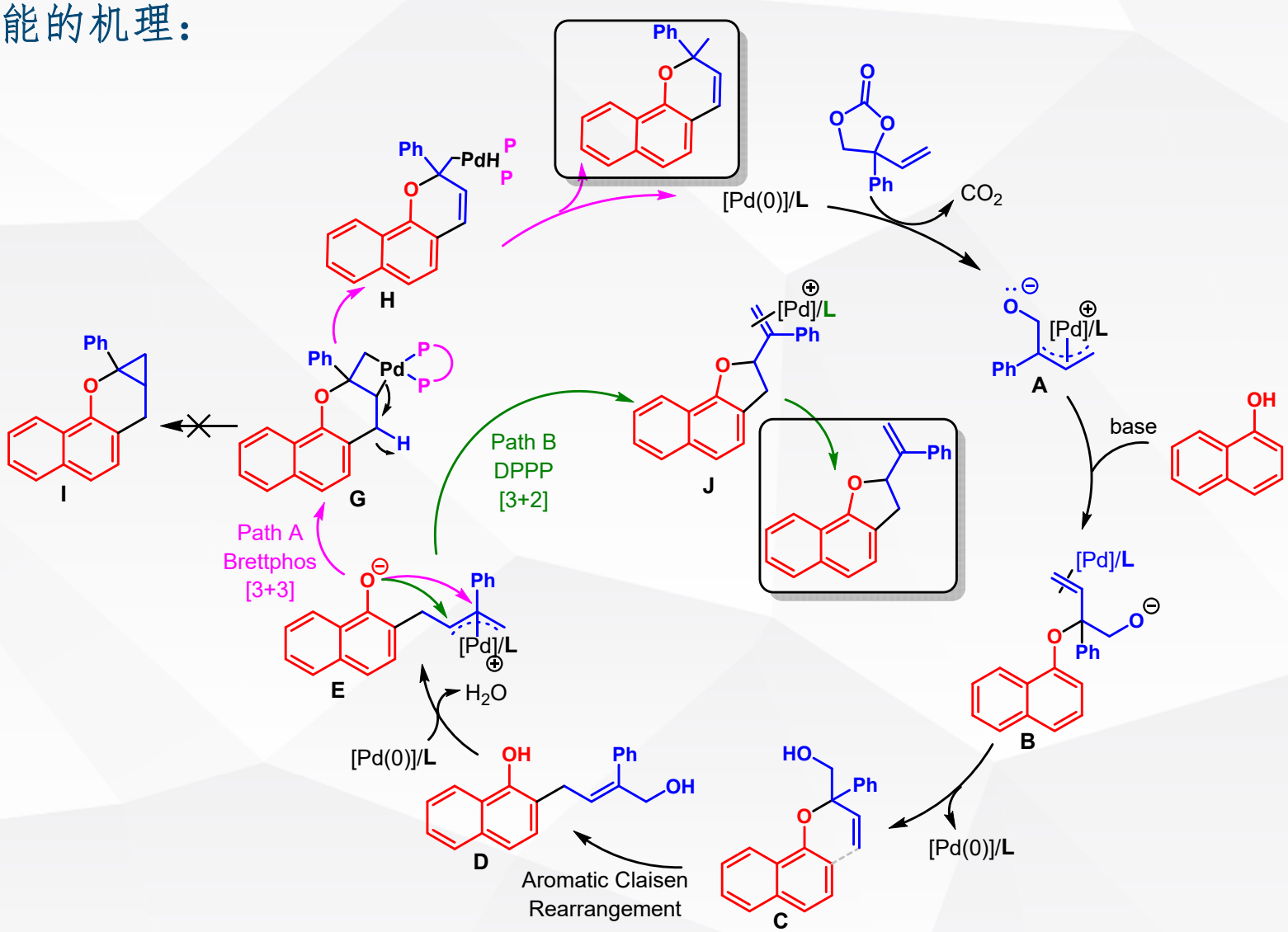
2.1 *C,O*-偶极子

配体控制的[3+2]环加成：



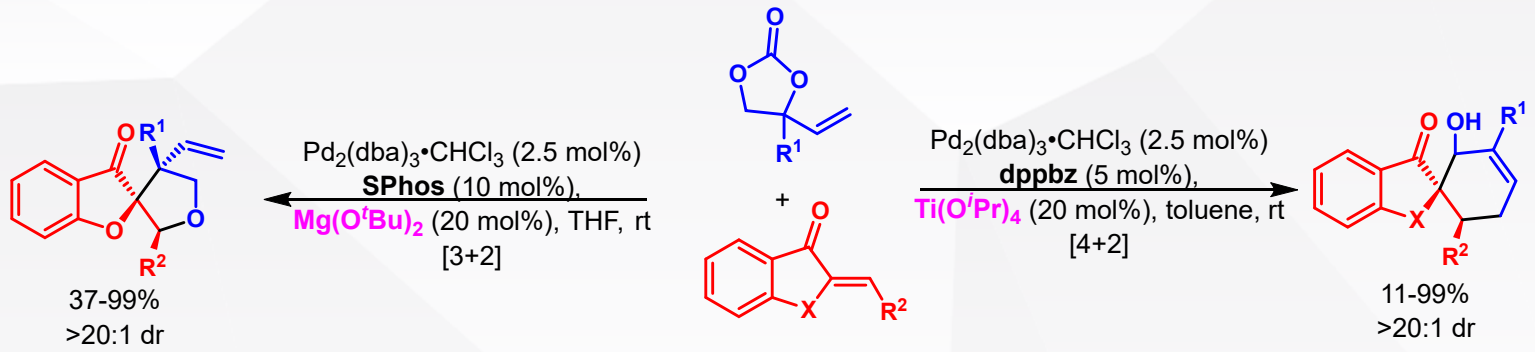
2.1 *C,O*-偶极子

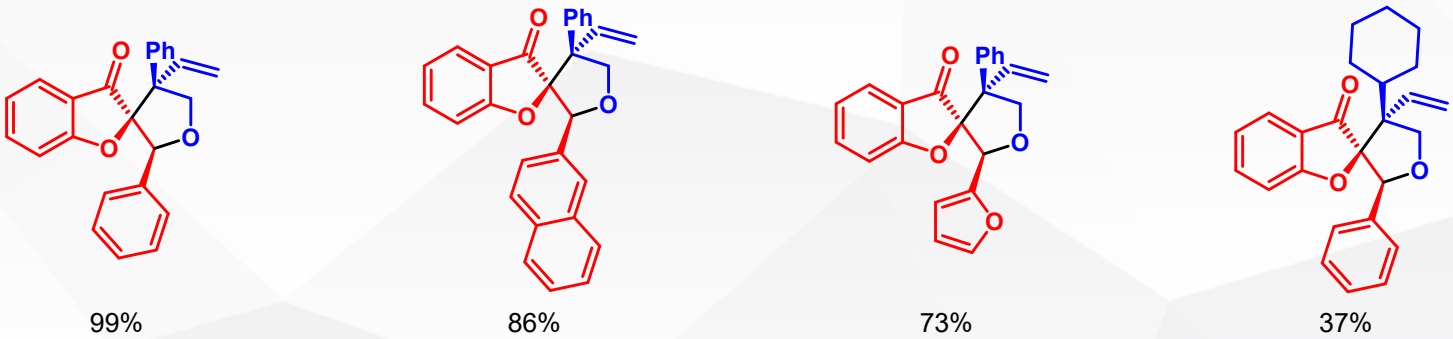
可能的机理：



2.1 *C,O*-偶极子

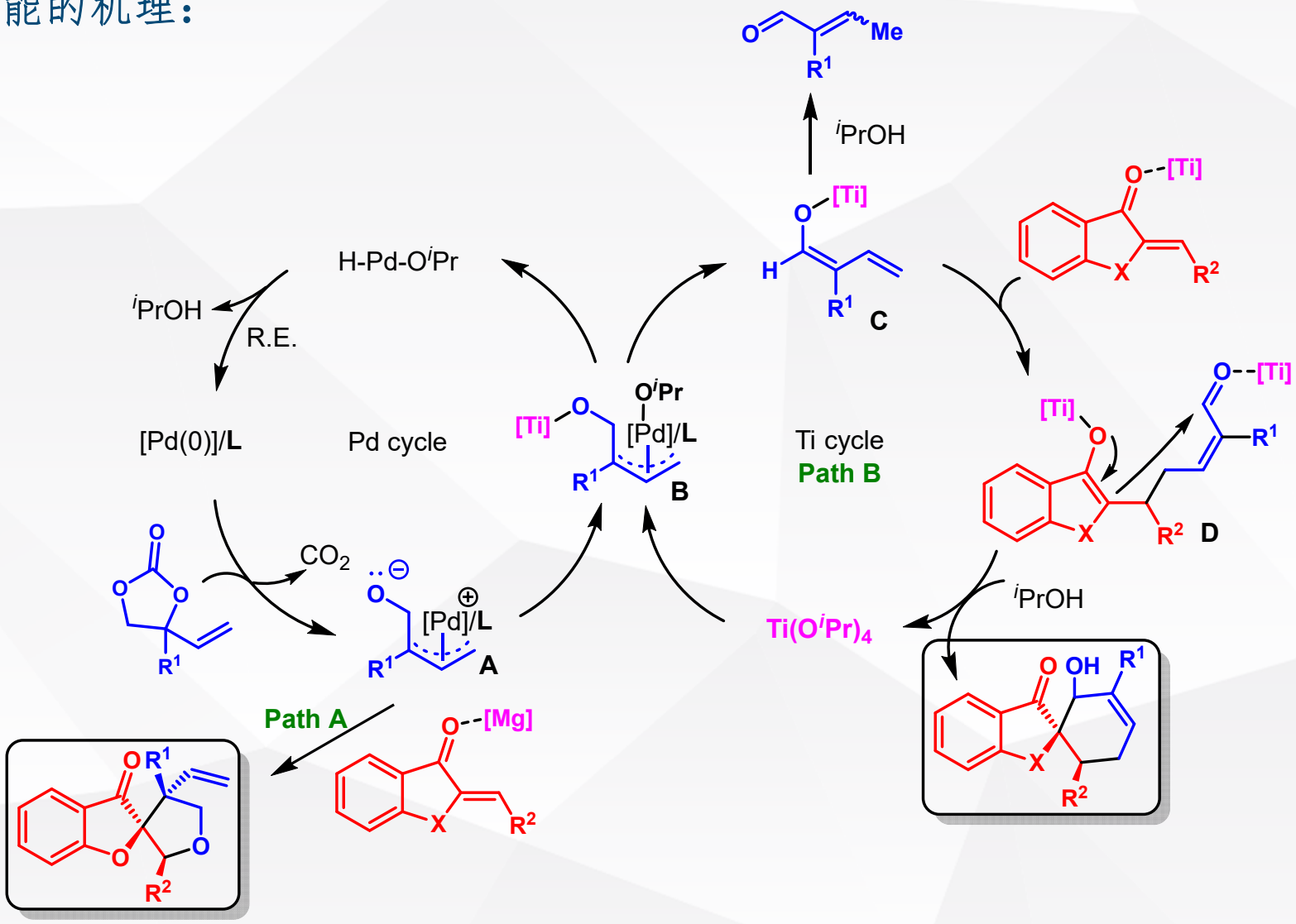
钯/路易斯酸协同催化：





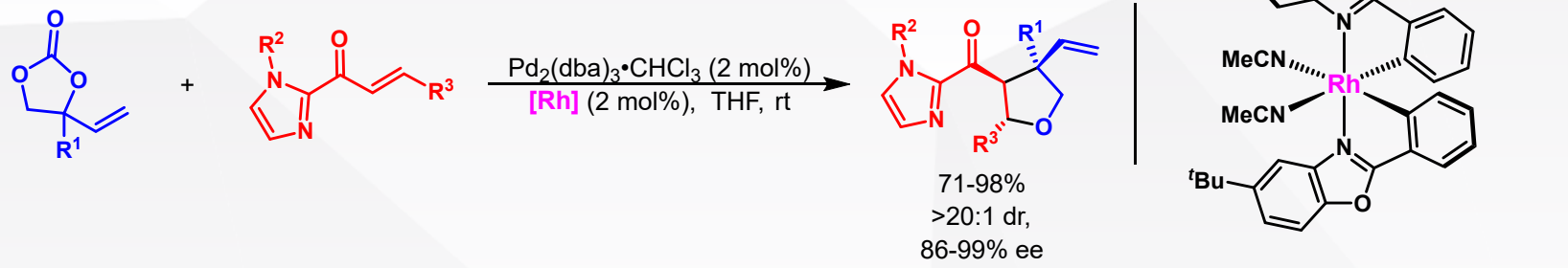
2.1 *C,O*-偶极子

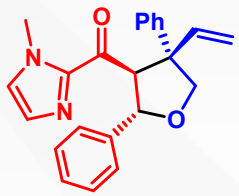
可能的机理：



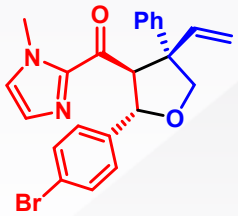
2.1 *C,O*-偶极子

双金属协同催化：

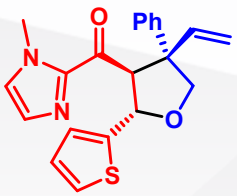




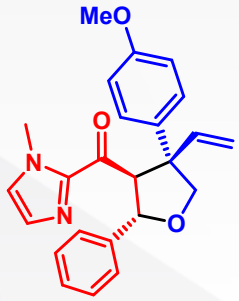
88%
>20:1 dr, 98% ee



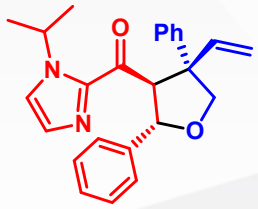
71%
>20:1 dr, 89% ee



78%
>20:1 dr, 86% ee



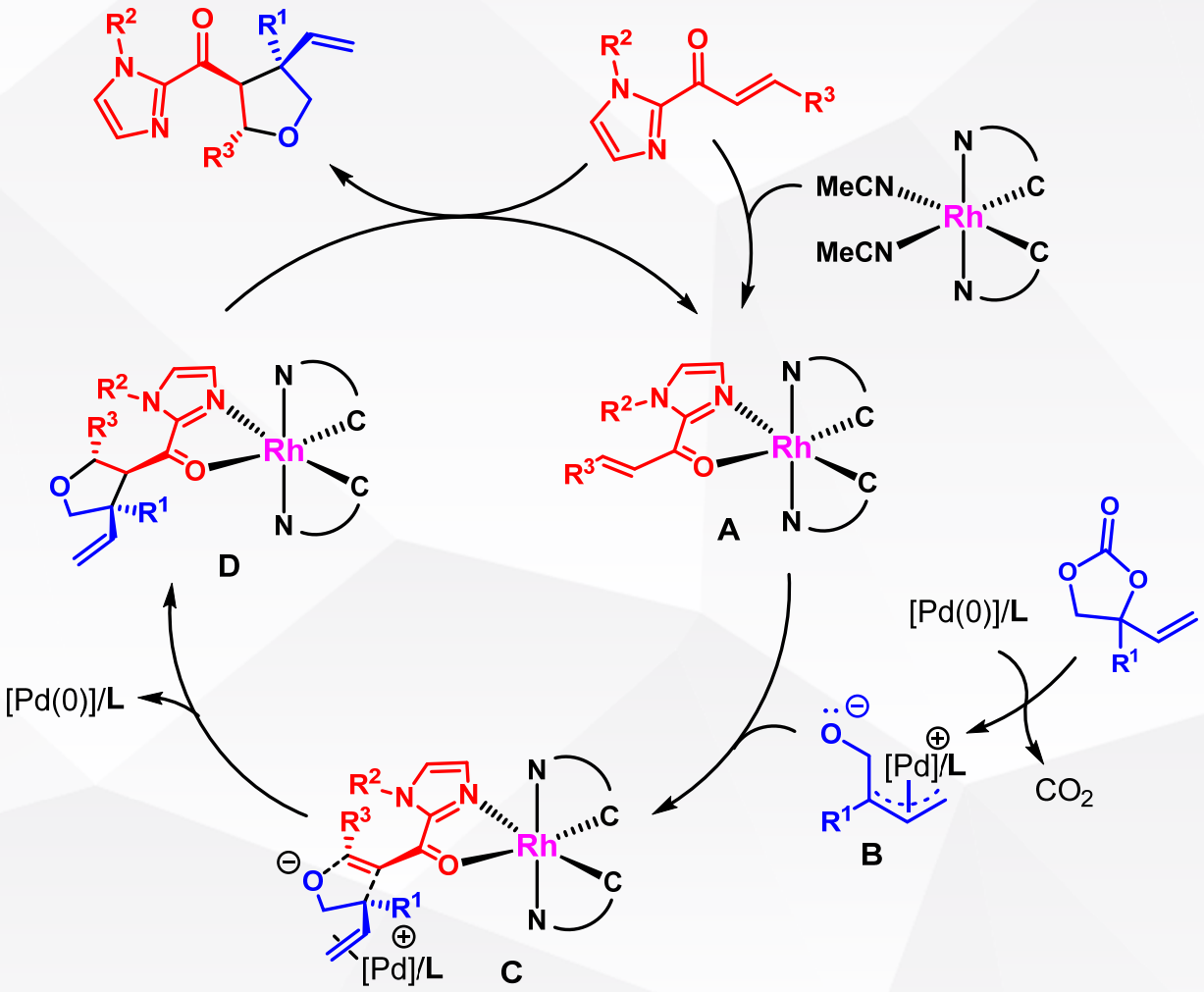
67%
>20:1 dr, 99% ee



81%
>20:1 dr, 96% ee

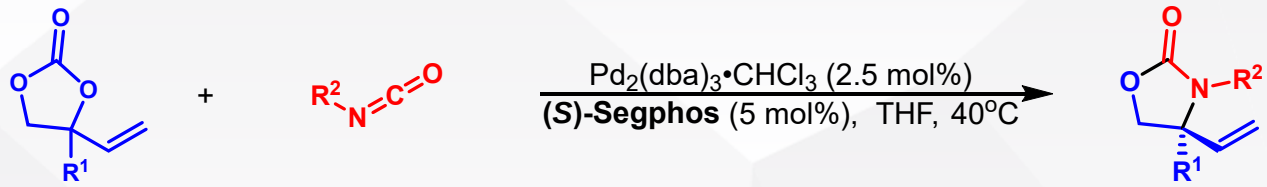
2.1 *C,O*-偶极子

可能的机理：



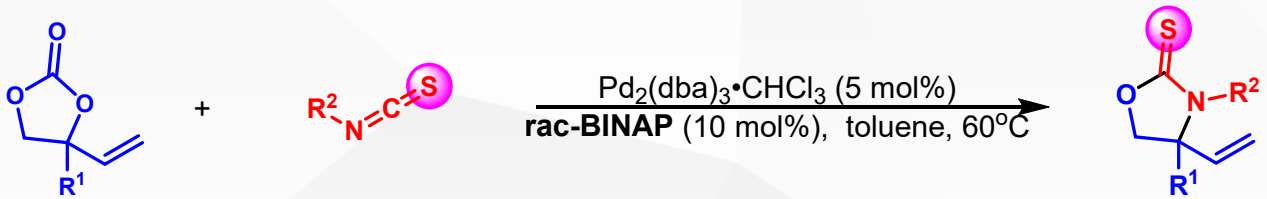
2.1 *C,O*-偶极子

异氰酸酯：



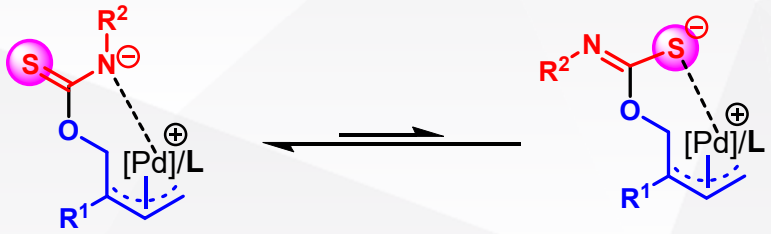
61-95%
37-99% ee

异硫氰酸酯：



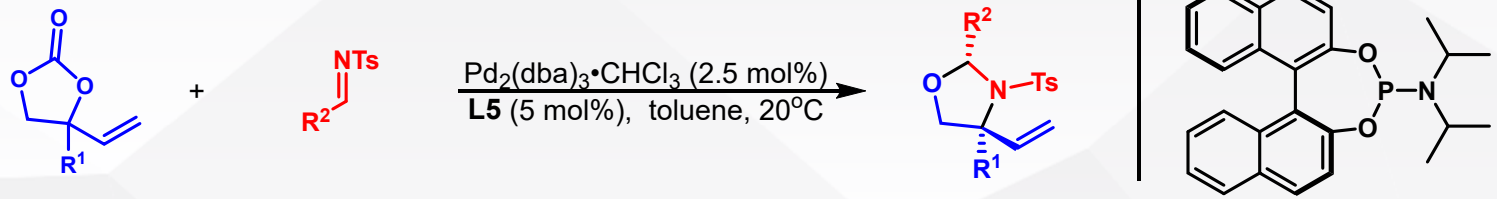
up to 94%

C-N Formation

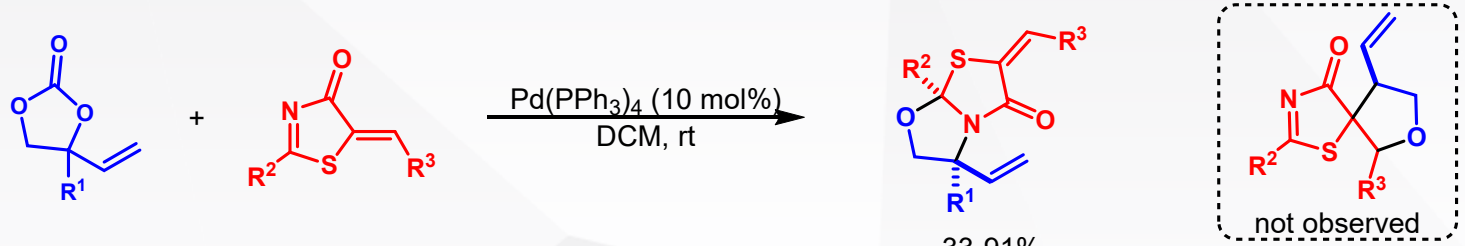


2.1 *C,O*-偶极子

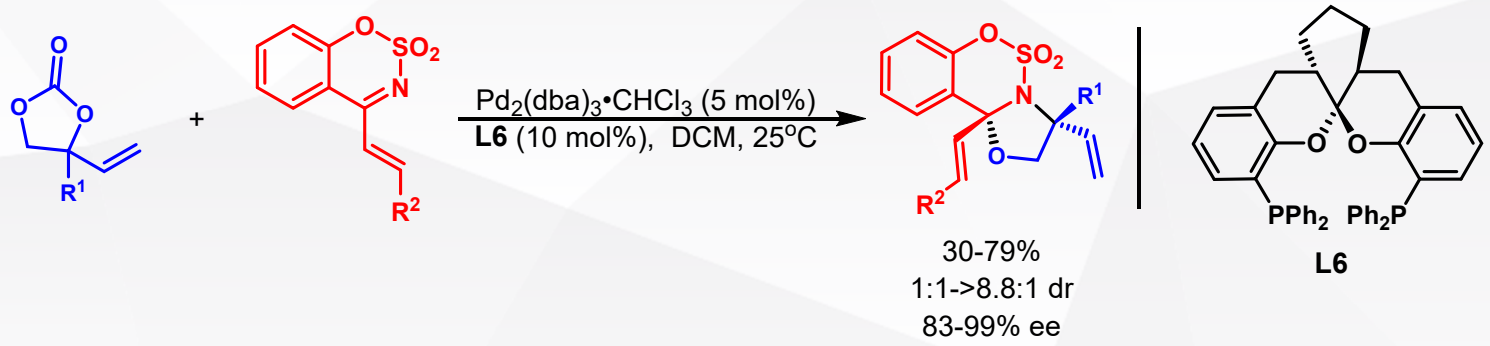
亚胺：



5-烯基噻唑酮：



环状N-磺酰基酮亚胺：



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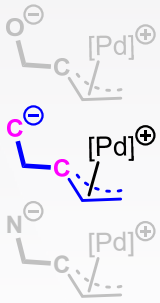
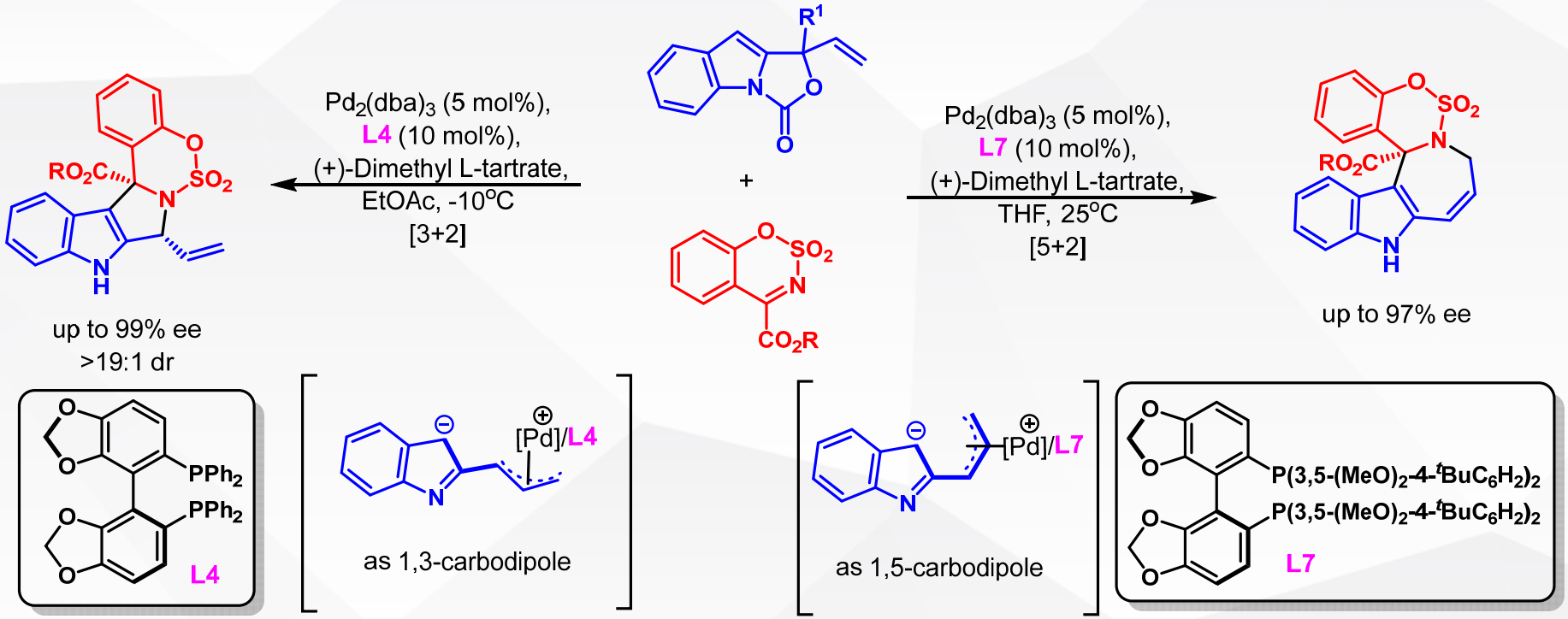
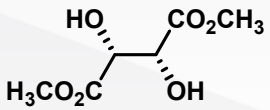


2.2 *C,C*-偶极子

配体控制：

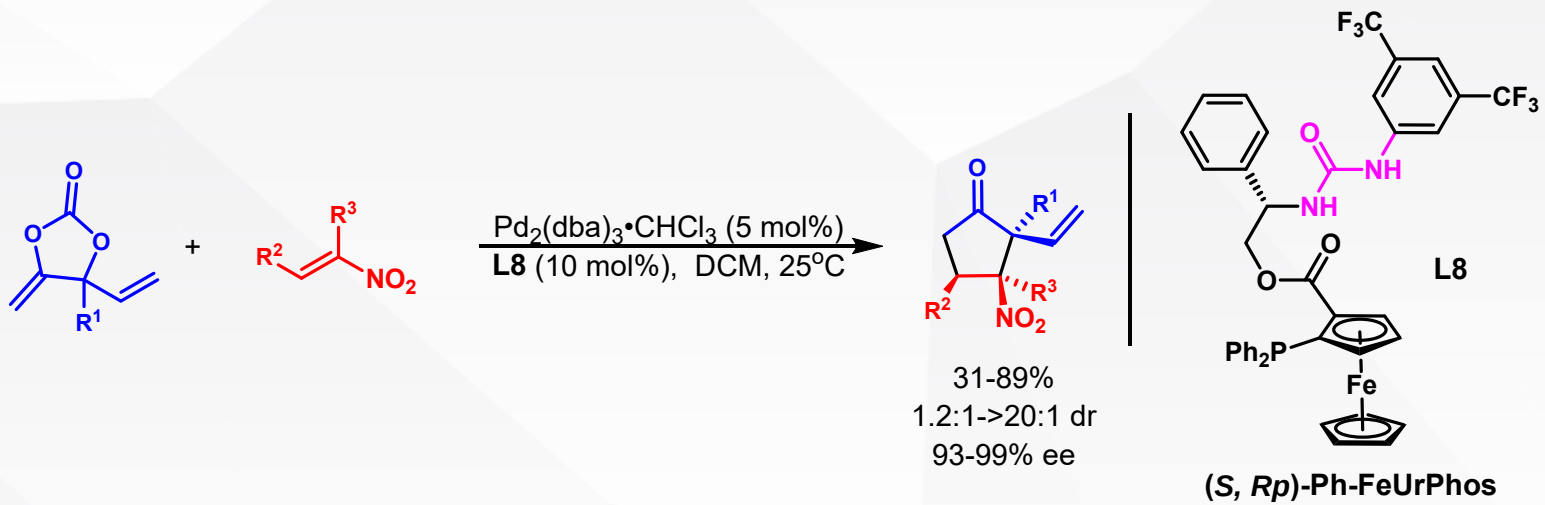


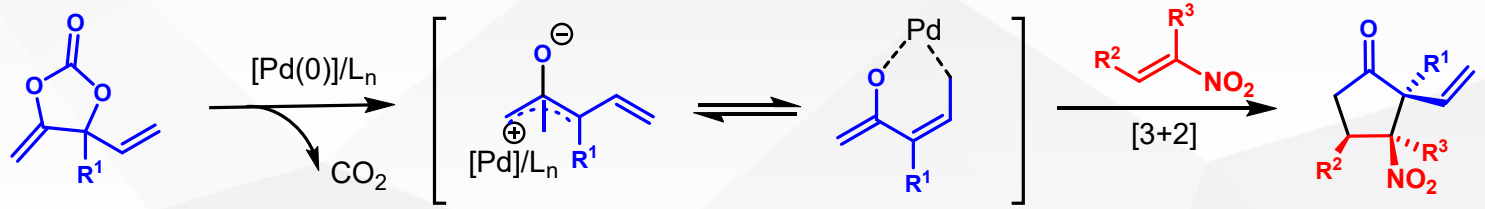
(+)-Dimethyl L-tartrate:



2.2 *C,C*-偶极子

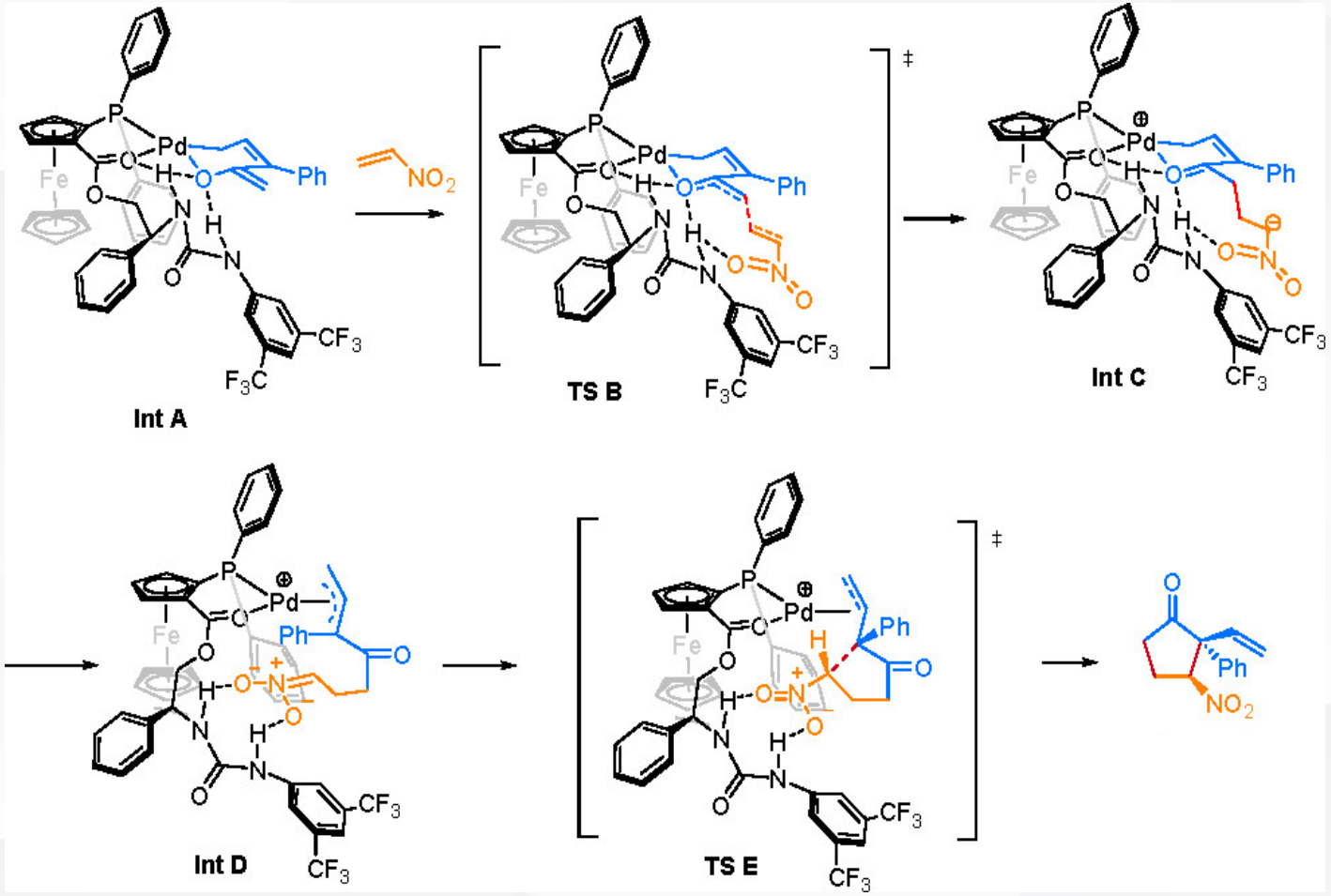
反向电子需求：





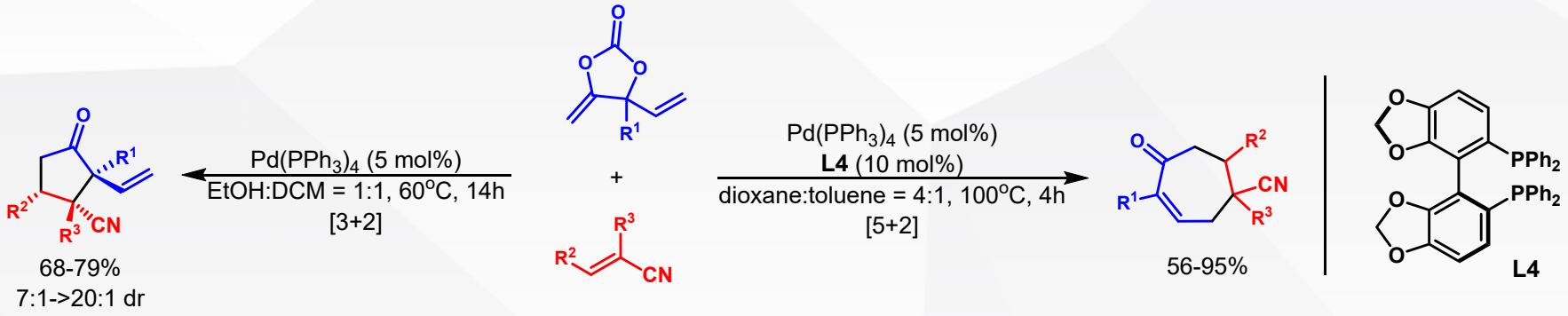
2.2 *C,C*-偶极子

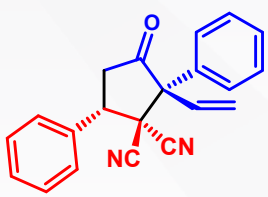
可能的机理：



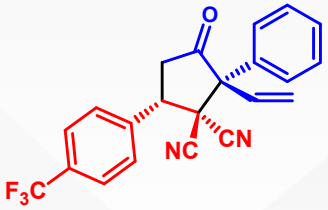
2.2 *C,C*-偶极子

Kinetically Controllable:

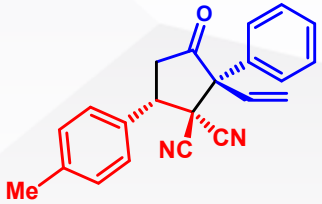




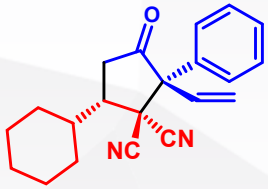
75%
16:1 dr



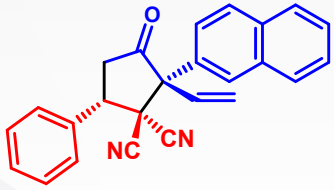
68%
7:1 dr



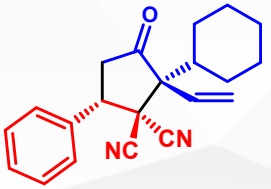
74%
9:1 dr



76%
16:1 dr



79%
>20:1 dr



78%
>20:1 dr

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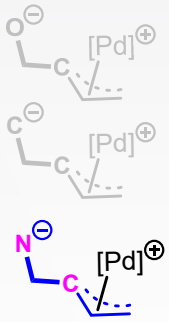
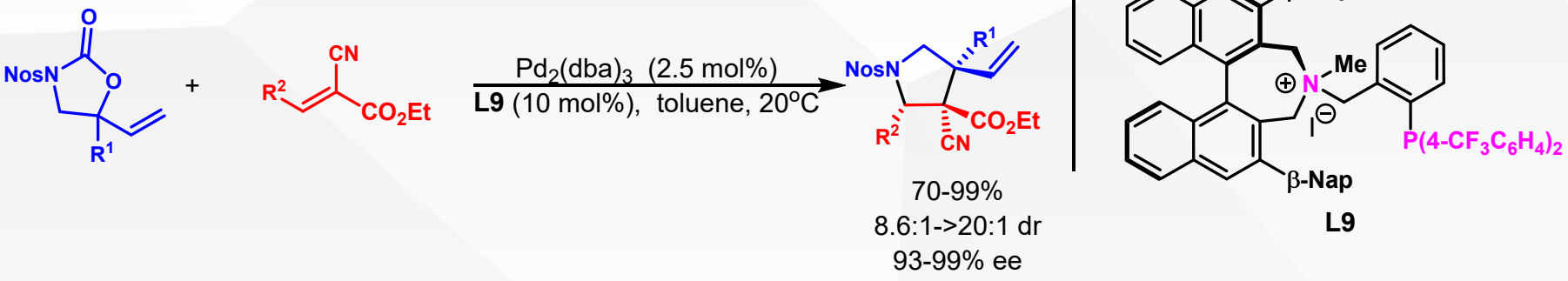
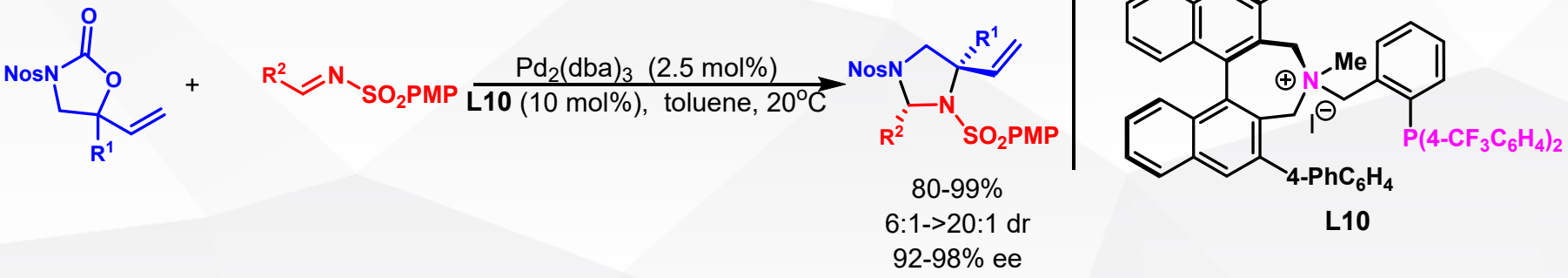


2.3 *C,N*-偶极子

氰基丙烯酸酯：

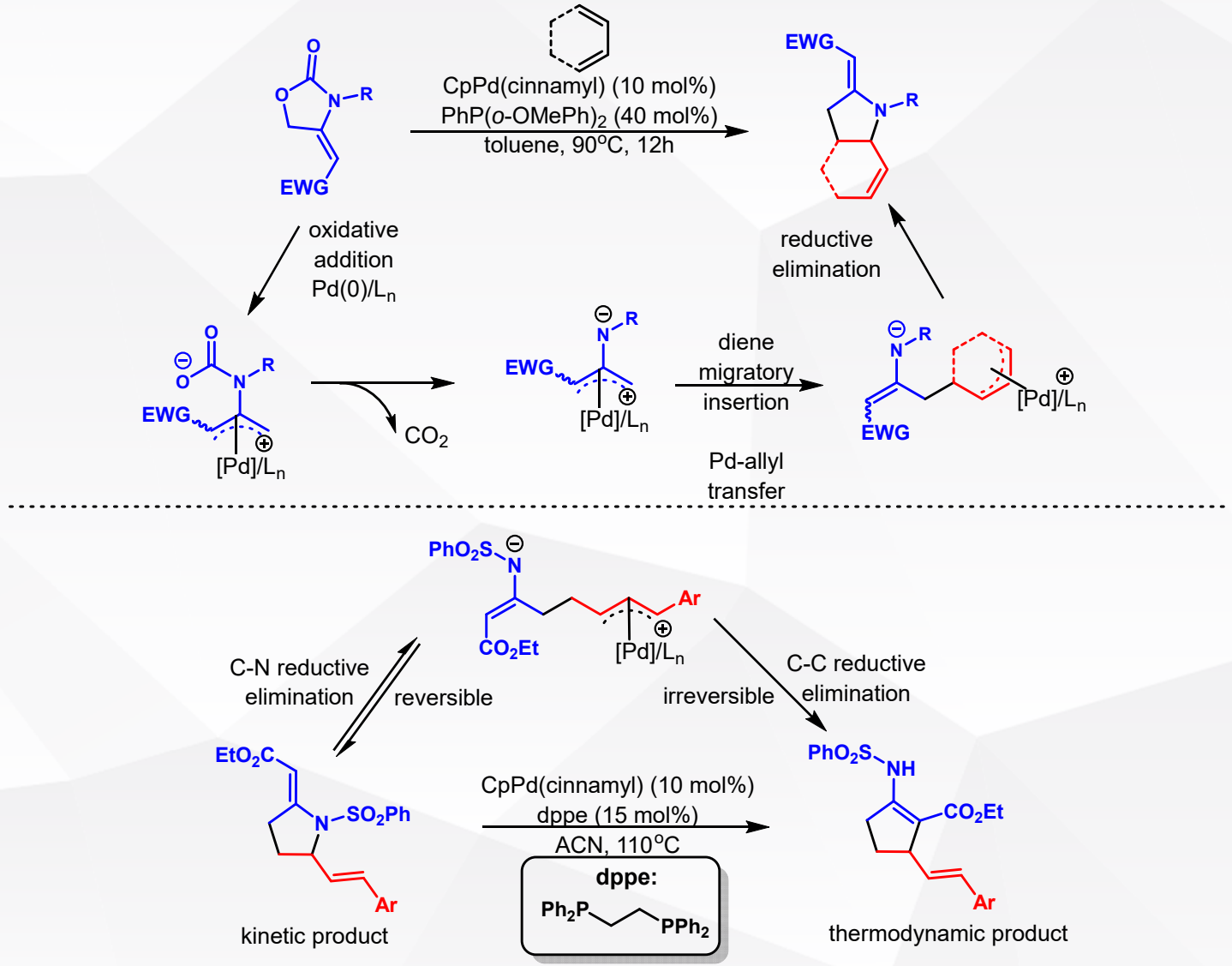


亚胺：



2.3 *C,N*-偶极子

氨基烯丙基钯与共轭二烯烃的环加成反应：



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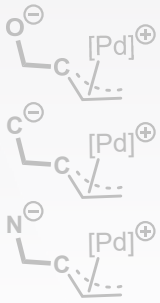
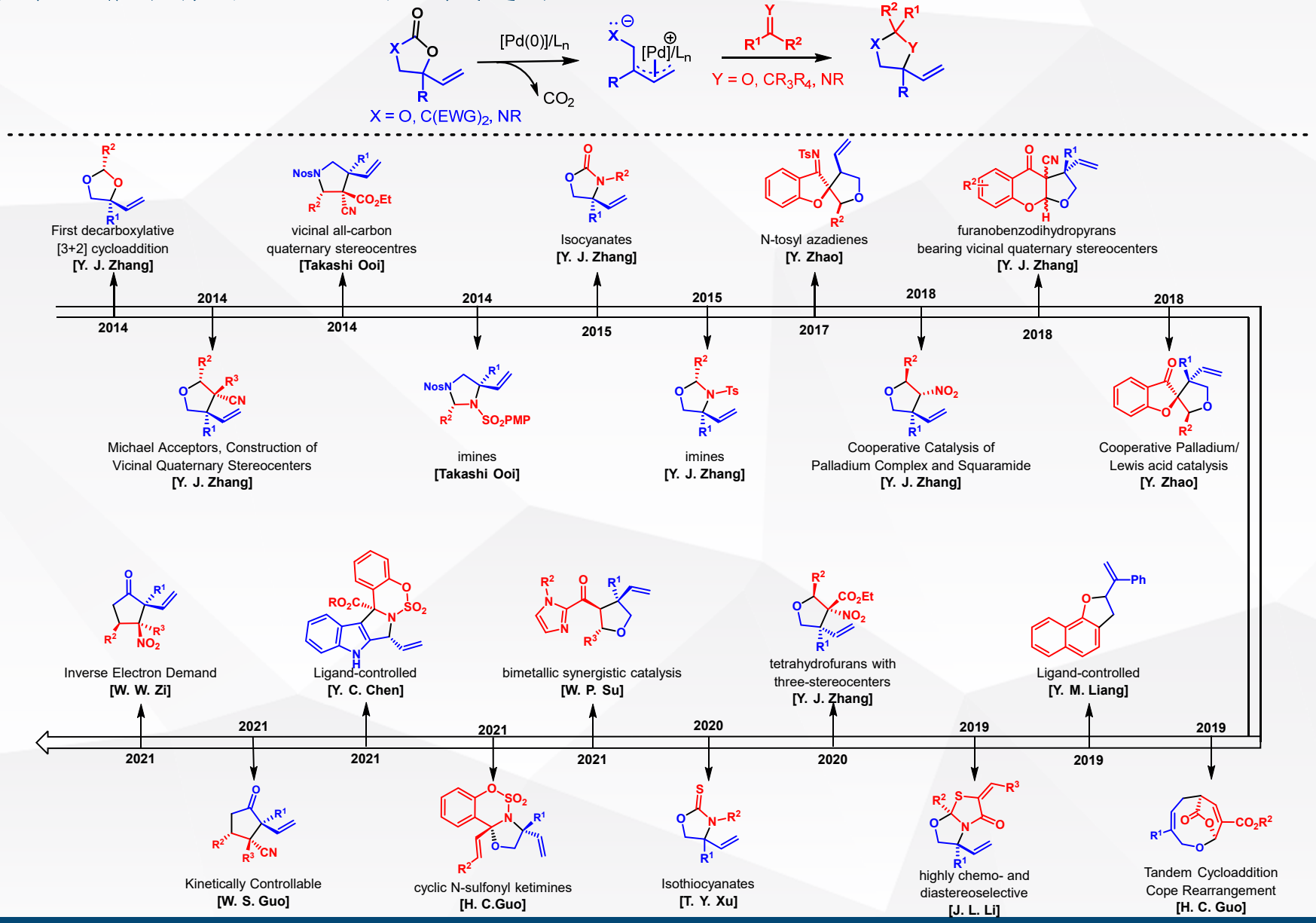
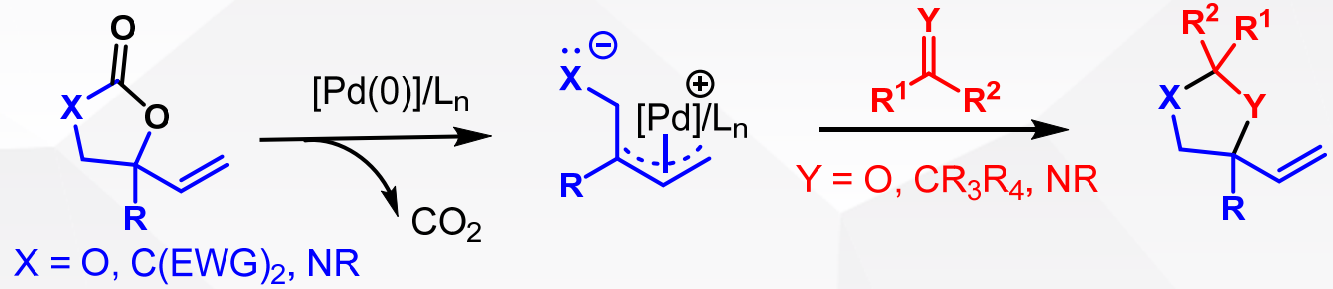


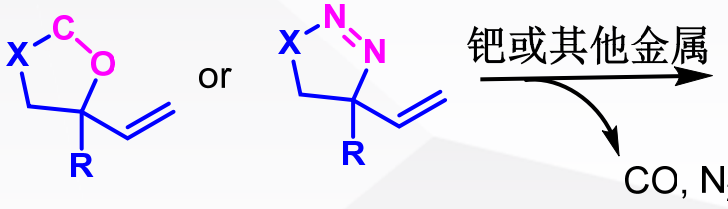
3. 总结与展望

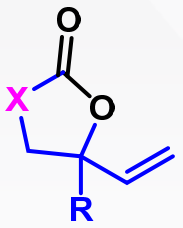
近年来钯催化脱酸[3+2]环加成总结：

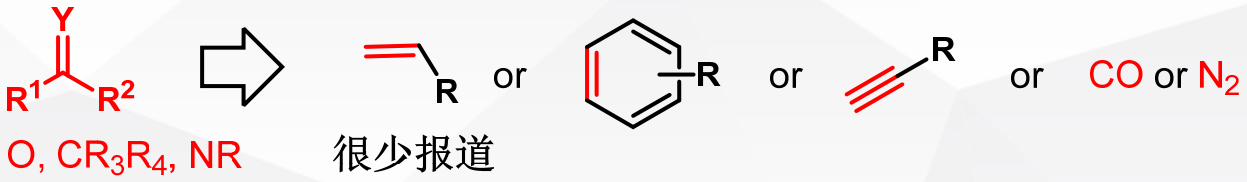


3. 总结与展望



1. 

2. 
X = S, Si(EWG)2, PR, P(O)R2

3. 

致谢

感谢陆老师的悉心指导，感谢施老师的关爱和开导，感谢实验室师兄、师姐对于我实验和日常的帮助，最后感谢中心的所有老师为我提供的指导和关心。

谢谢