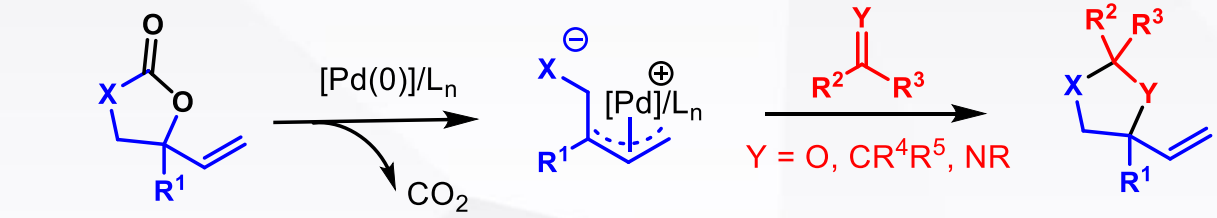
钯催化VECs的脱羧[3+2]环加成反应



汇报人 ： 潘仁明
导师 ： 陆平 研究员

2022-06-10

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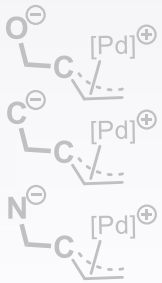
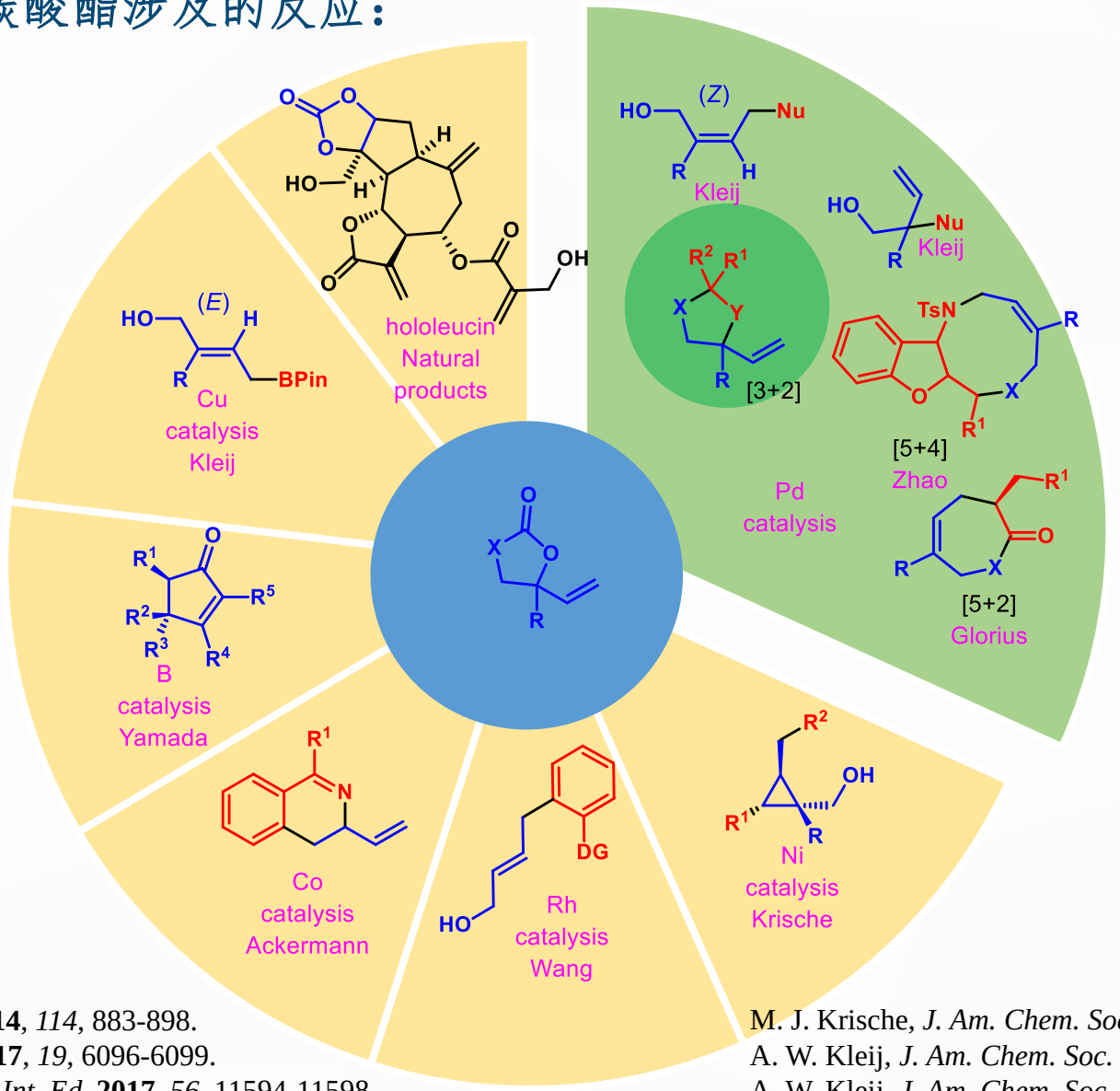


1. 背景

近年来乙烯基碳酸酯涉及的反应：

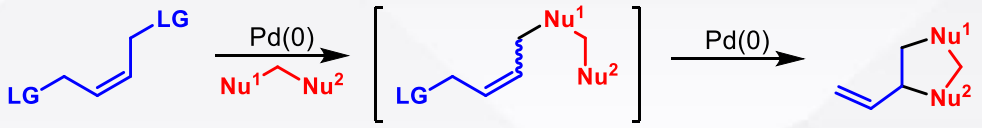


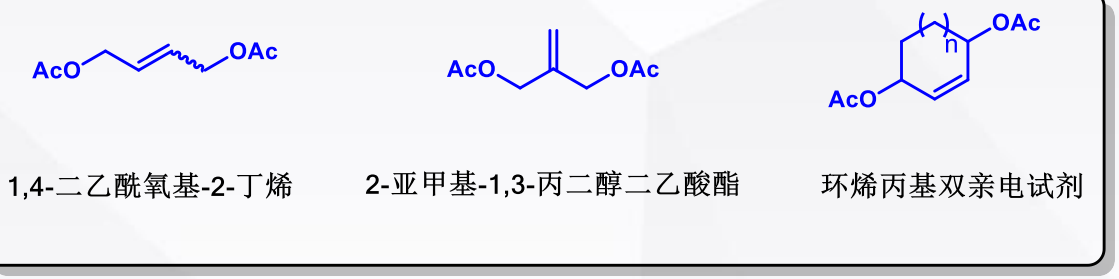
J. M. Yue, *Chem. Rev*. **2014**, *114*, 883-898.
A. W. Kleij, *Org. Lett.* **2017**, *19*, 6096-6099.
T. Yamada, *Angew.Chem. Int .Ed.* **2017**, *56*, 11594-11598.
L. Ackermann, *ACS Catal.* **2015**, *7*, 3430-3433.
H. Wang, *ACS Catal.* **2015**, *5*, 210-214.
M. J. Krische, *J. Am. Chem. Soc.* **2017**, *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

钯催化生成偶极子模型：

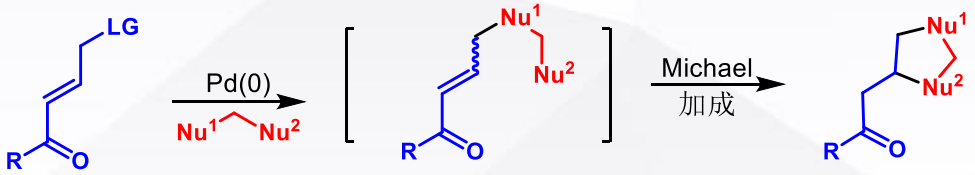
1) 双烯丙基体系生成的偶极子:

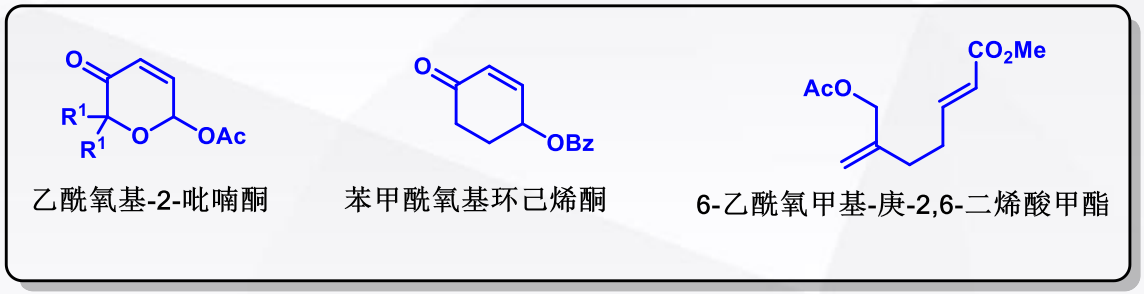




J. Tsuji, *Tetrahedron Lett.* **1965**, *49*, 4387-4388. B. Trost, *J. Am. Chem. Soc.* **1973**, *95*, 292-294. B. Trost, *Acc. Chem. Res.* **1980**, *13*, 385-393.

2) 带有烯丙基离去基团的Michael受体生成的偶极子:



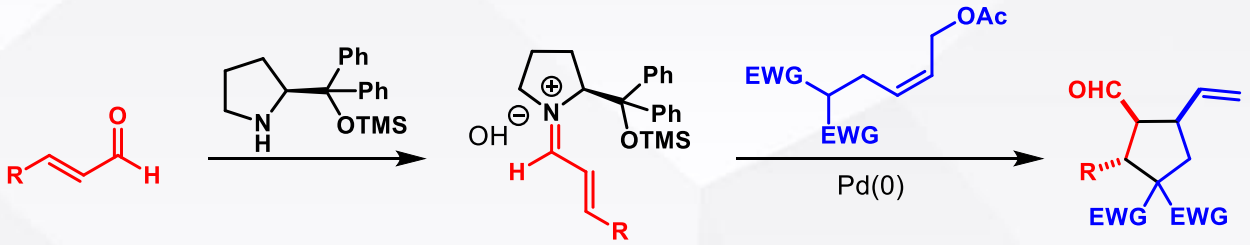


B. Trost, *Chem Rev.* **2003**, *103*, 2921-2944. C. Jousse, *Eur. J. Org. Chem.* **2001**, *2001*, 3631-3640. J. Yu, *Org, Chem. Front.* **2016**, *3*, 714-719.

1. 背景

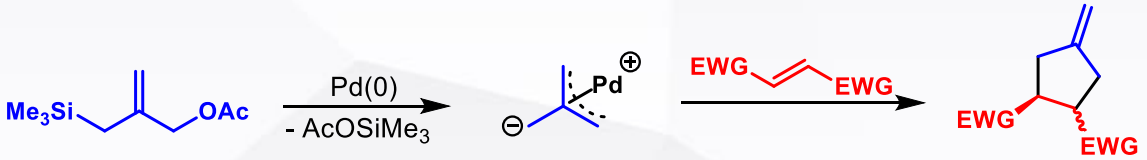
钯催化生成偶极子模型：

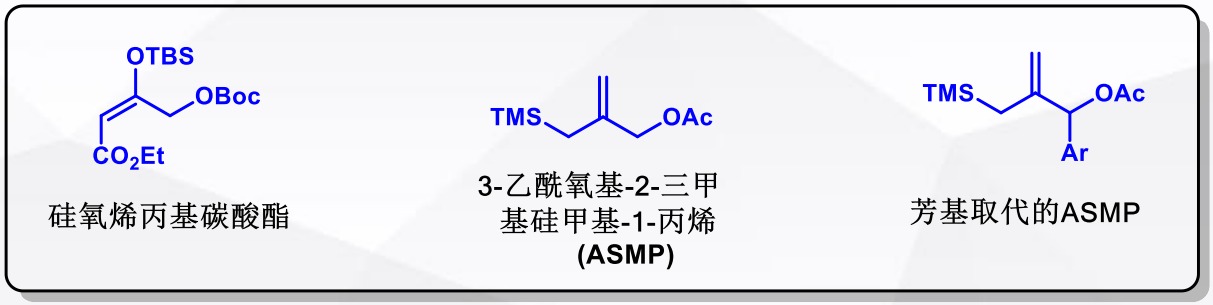
3) 有机催化剂生成的亲偶极子:



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：



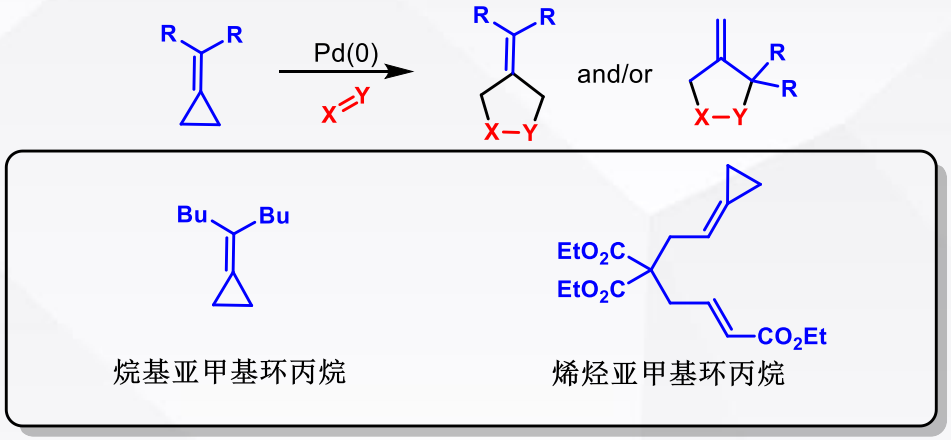


M. Lautens, *Chem. Rev.* **1996**, *96*, 49-92. B. Trost, *Pure. Appl. Chem.* **1988**, *60*, 1615-1626.;
S. Yamago, *Org. React.* **2003**, *61*, 1-217. I. Kumar, *RSC Adv.* **2014**, *4*, 16397-16408.

1. 背景

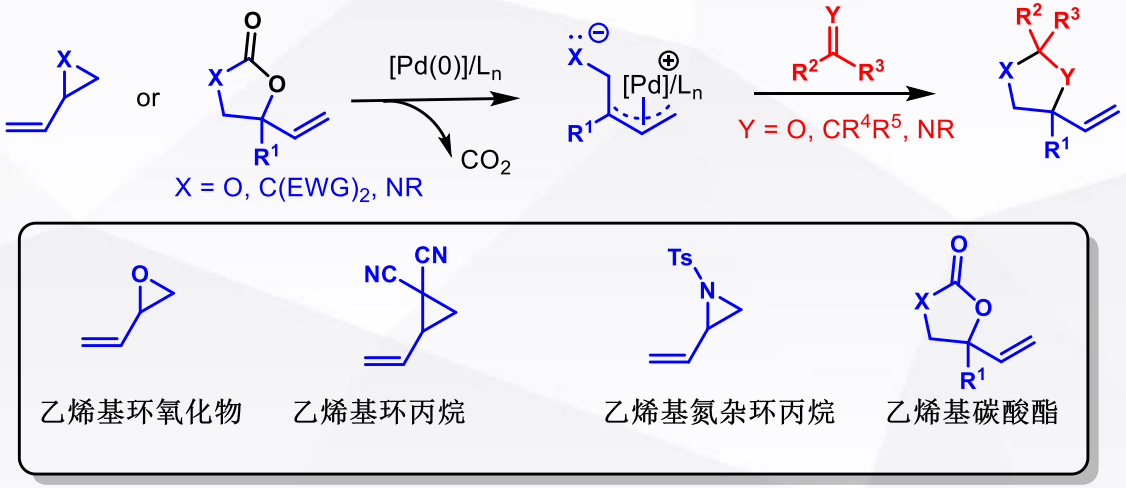
钯催化生成偶极子模型：

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.

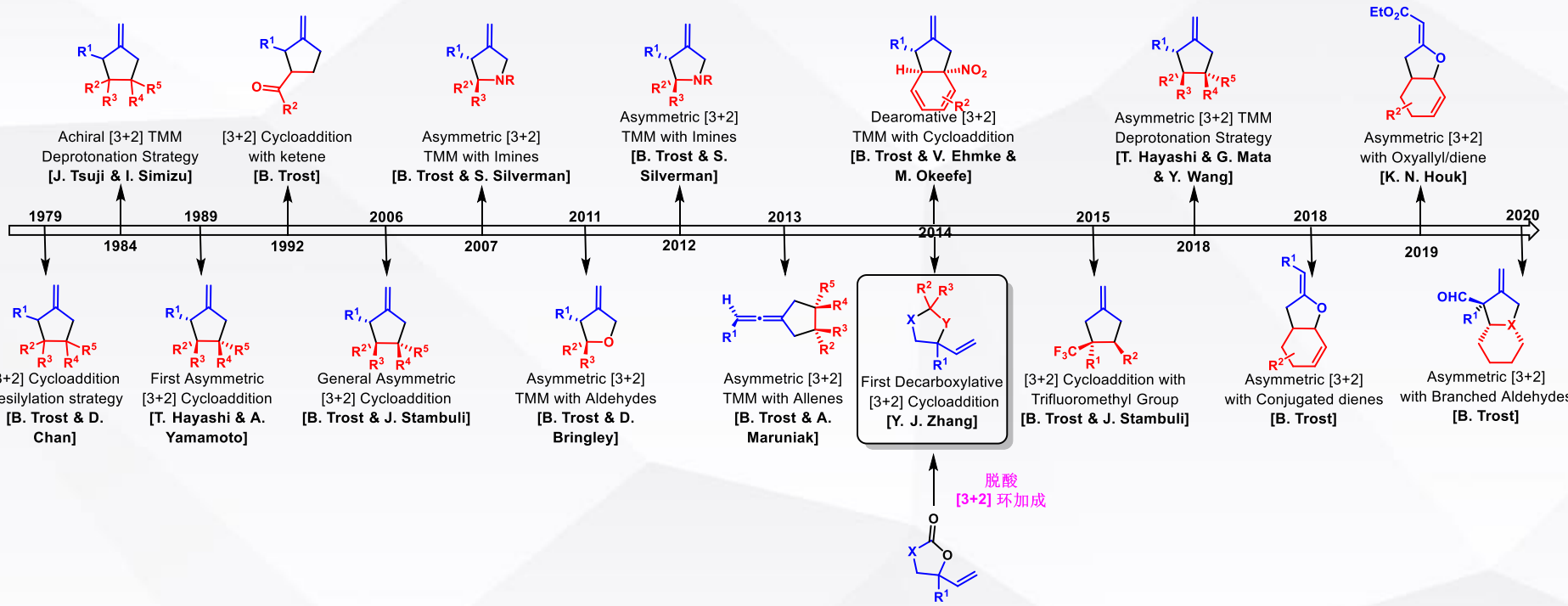
6) 乙烯基环杂丙烷或乙烯基碳酸脂类作为异偶极子:



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.
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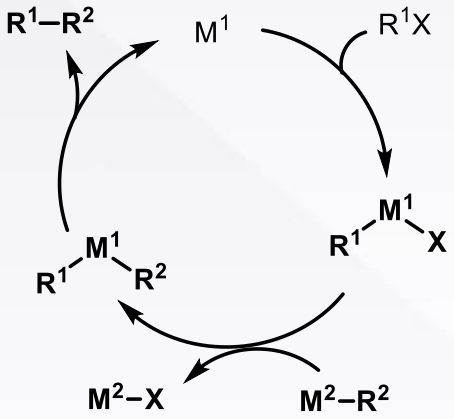
B. Trost, *Org. Lett.* **2014**, *16*, 2708-2710. Y. J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 6439-6442. B. Trost, *Org. Lett.* **2018**, *20*, 39388-3940.
K. N. Houk, *J. Am. Chem. Soc.* **2019**, *141*, 12382-12387. G. Poli**,** *Eur. J. Inorg. Chem.* **2020**, *20*, 942-961.
B. Trost, *Narure Chemistry*, **2020**, *12*, 294-301. B. Trost, *Acc. Chem. Res.* **2020**, *53*, 1293-1305.

1. 背景

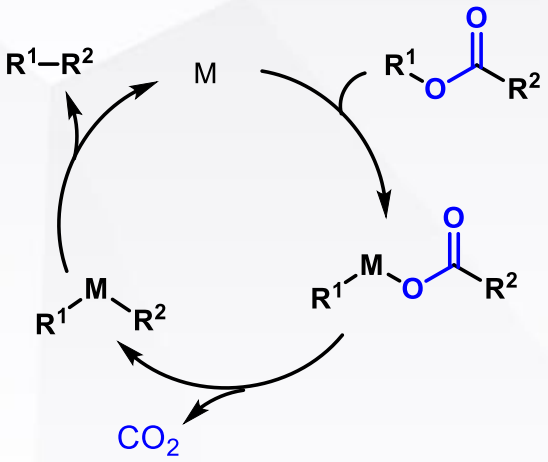
常见交叉偶联与脱羧偶联对比：

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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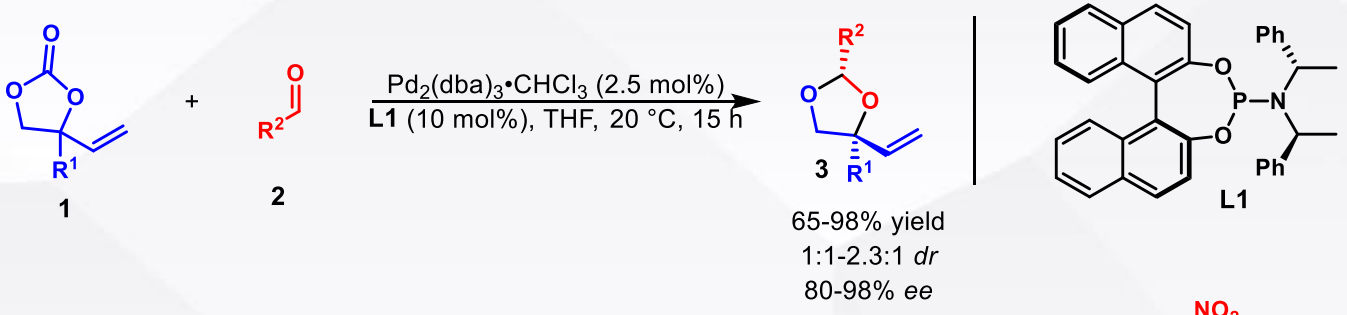
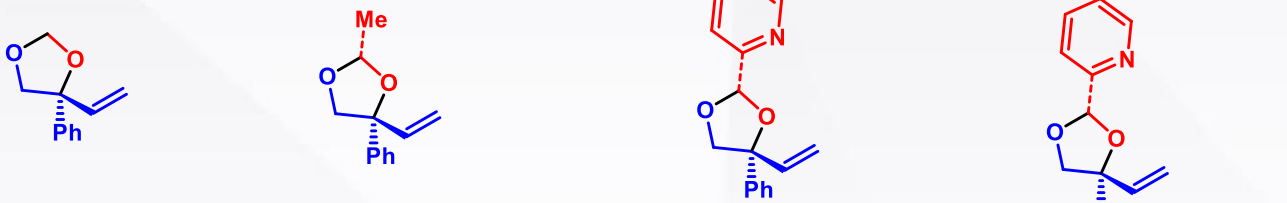
2.1 *C,O*-偶极子

首次实现脱羧[3+2]环加成：



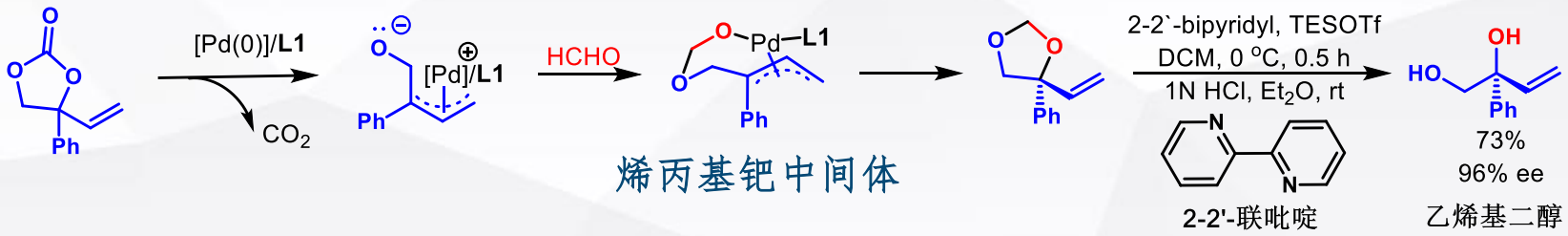


96% yield
96% *ee*

86% yield, *cis/trans* = 1:1
75% *ee* / 87% *ee*

91% yield, *cis/trans* = 2:1
91% *ee* / 95% *ee*

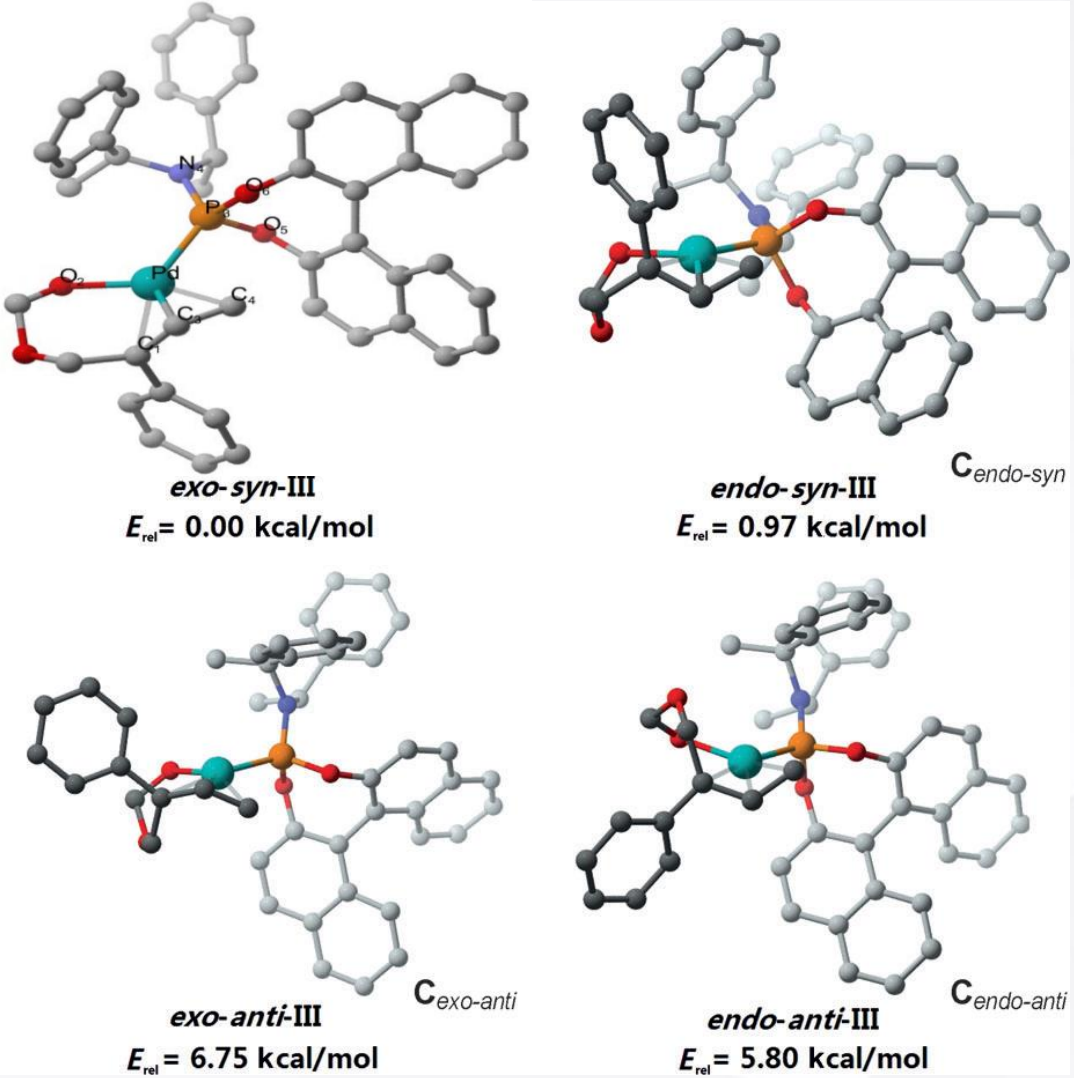
89% yield, *cis/trans* = 2.3:1
98% *ee* / 95% *ee*



烯丙基钯中间体

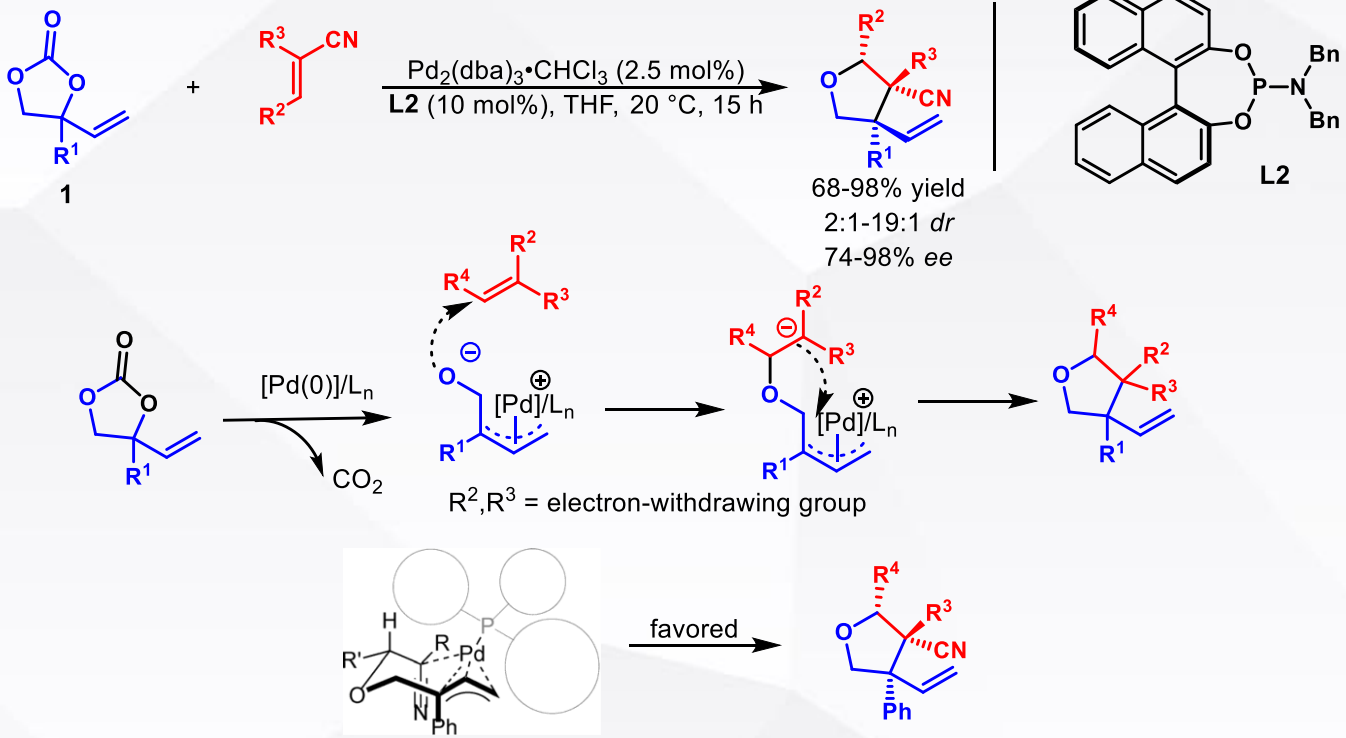
2.1 *C,O*-偶极子

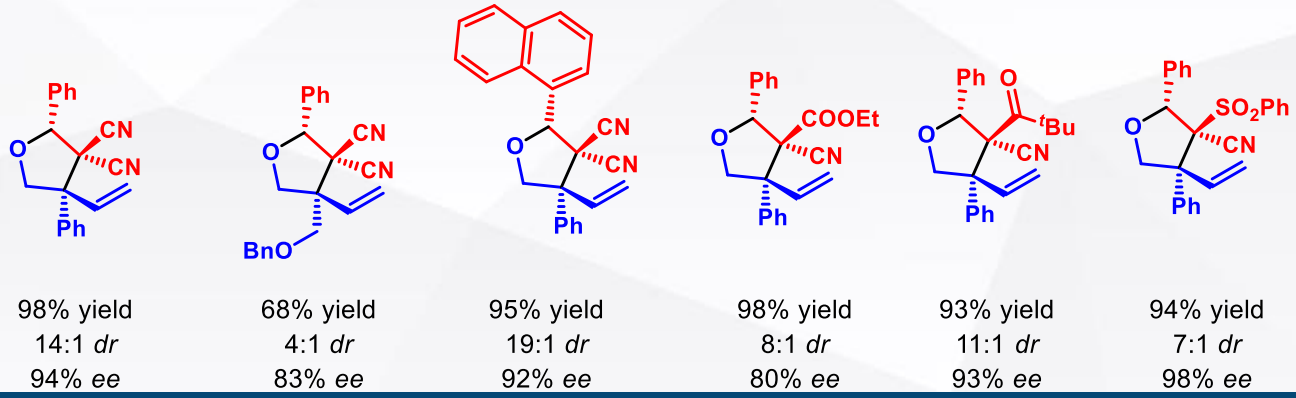
钯中间体的四种可能异构体的计算结构及其相对能量:



2.1 *C,O*-偶极子

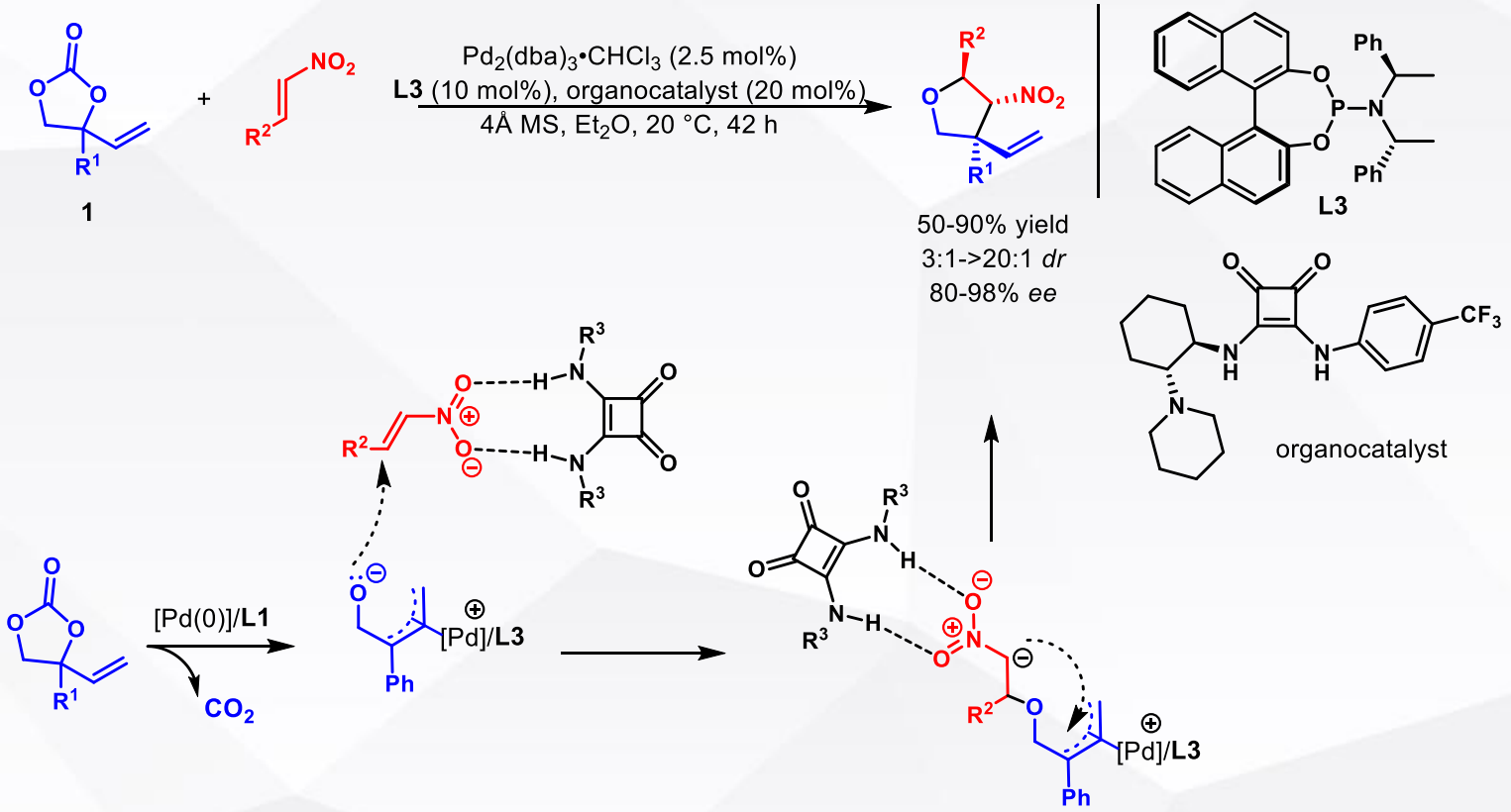
Michael受体生成的相邻季碳立体中心的构建：





2.1 *C,O*-偶极子

钯络合物与方酰胺的协同催化作用：

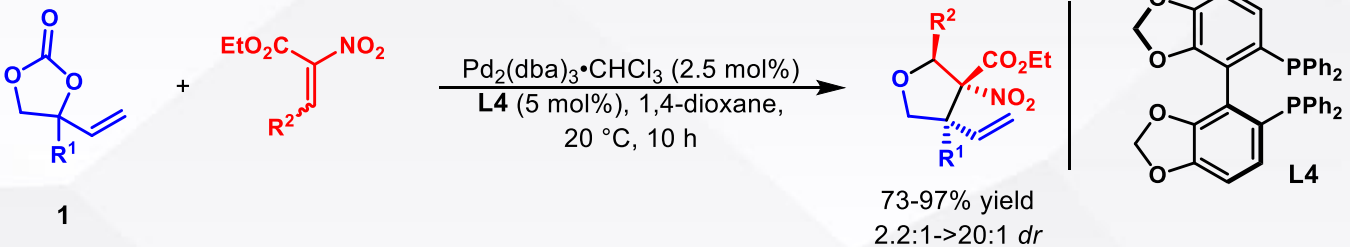


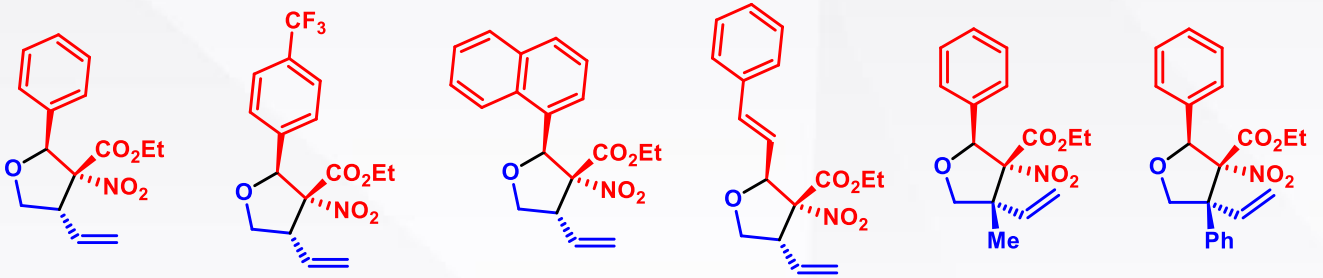
entry	ligand	OC	solvent	yield	*ee* (%)	*dr*
1	L3	-	THF	70	75	20:1
2	L3	20 mol%	THF	63	83	20:1

Y. J. Zhang, *ACS Catal.* **2018**, *38*, 11600-11604.

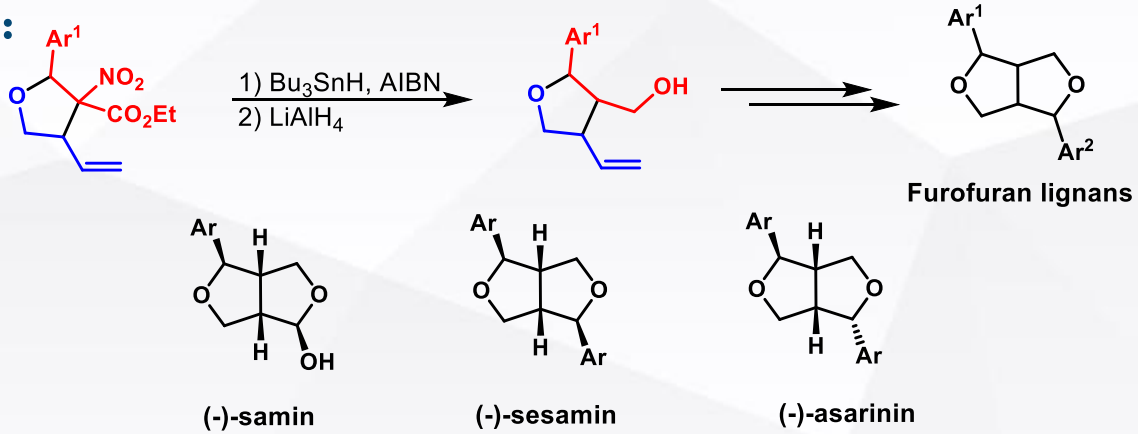
2.1 *C,O*-偶极子

三个连续立体中心的四氢呋喃类化合物的构建：



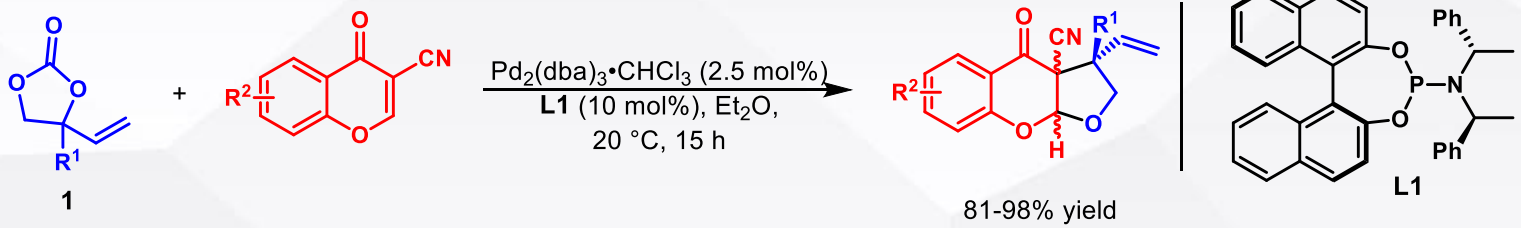


呋喃木质素的合成：

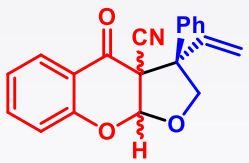


2.1 *C,O*-偶极子

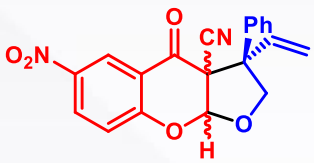
相邻季碳立体中心的呋喃二氢吡喃类化合物的构建：



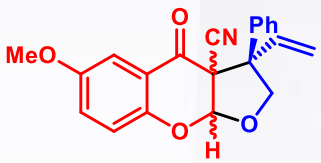
81-98% yield
1:1.3-7.5:1 *dr*
96-98% *ee*



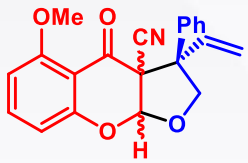
98% yield, 2.1:1 *dr*
96% *ee*, 94% *ee*



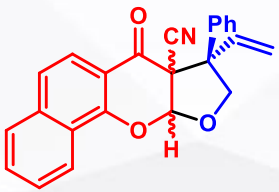
92% yield, 1:1 *dr*
78% *ee*, 61% *ee*



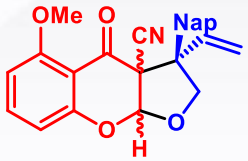
90% yield, 3.8:1 *dr*
96% *ee*, 91% *ee*



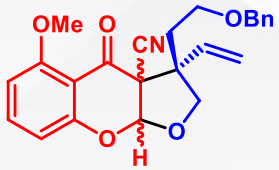
92% yield, 4.2:1 *dr*
97% *ee*, 95% *ee*



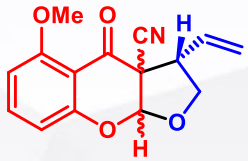
92% yield, 3.9:1 *dr*
95% *ee*, 90% *ee*



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



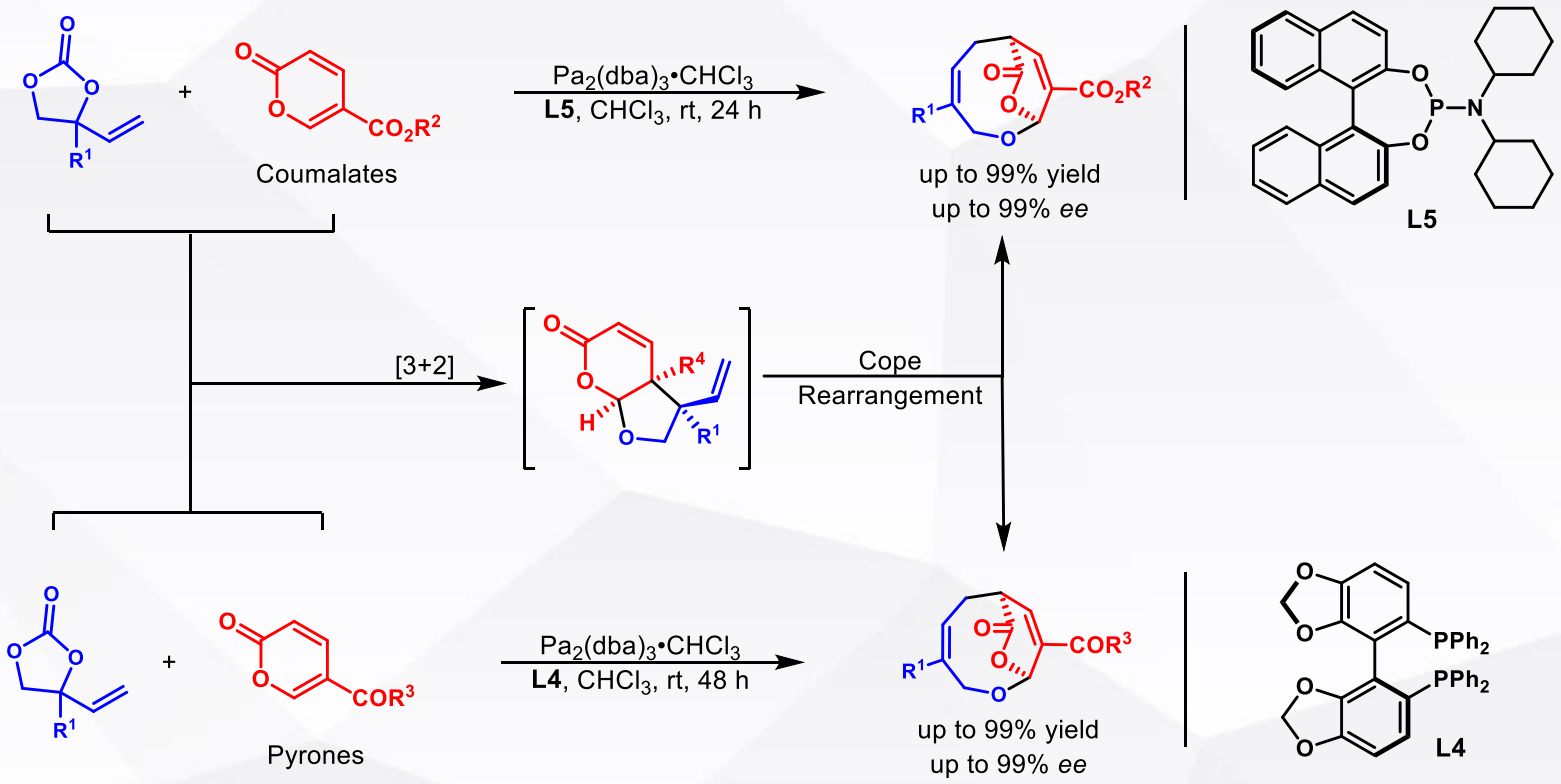
88% yield, 3.4:1 *dr*
94% *ee*, 87% *ee*



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

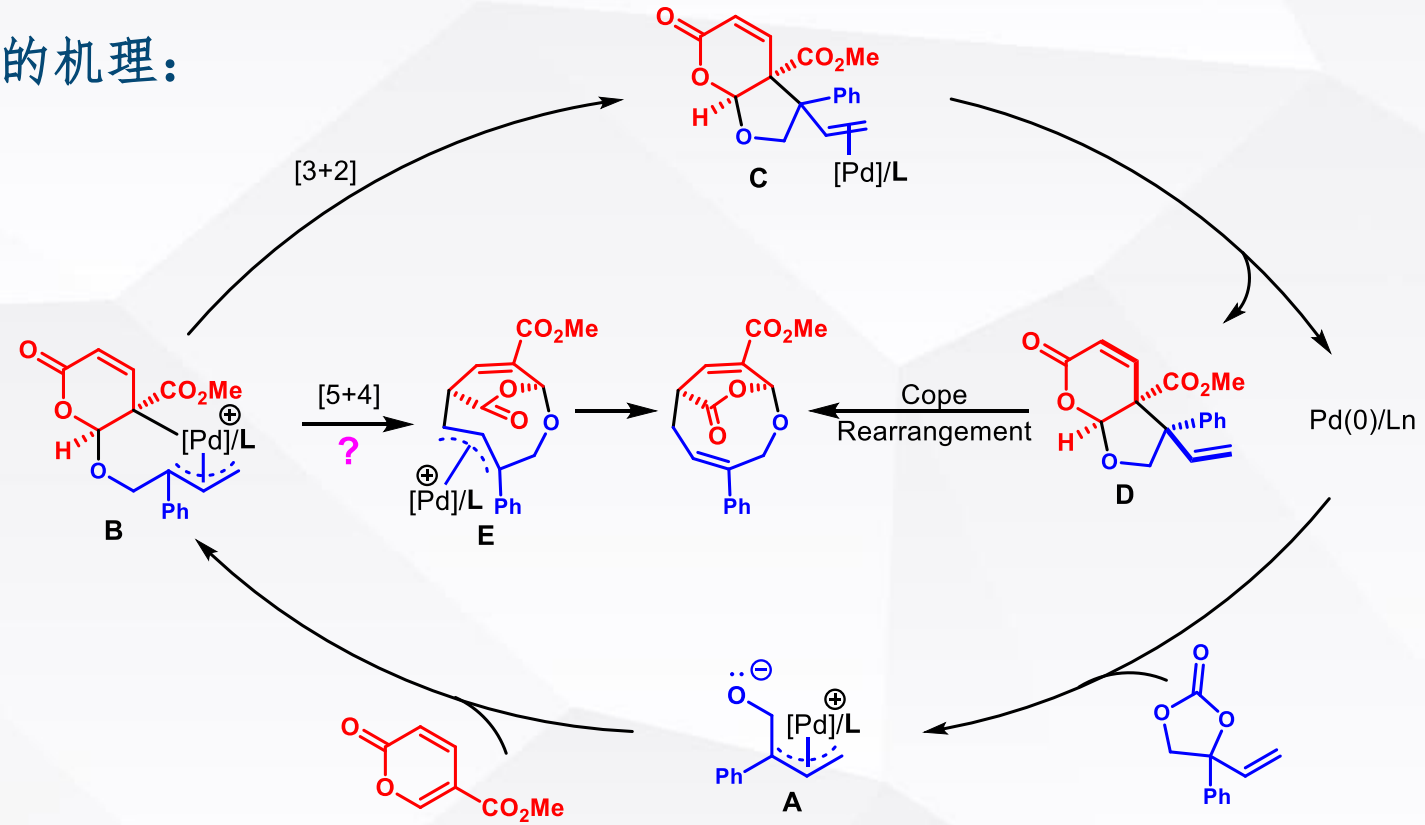
2.1 *C,O*-偶极子

串联环加成和Cope重排：

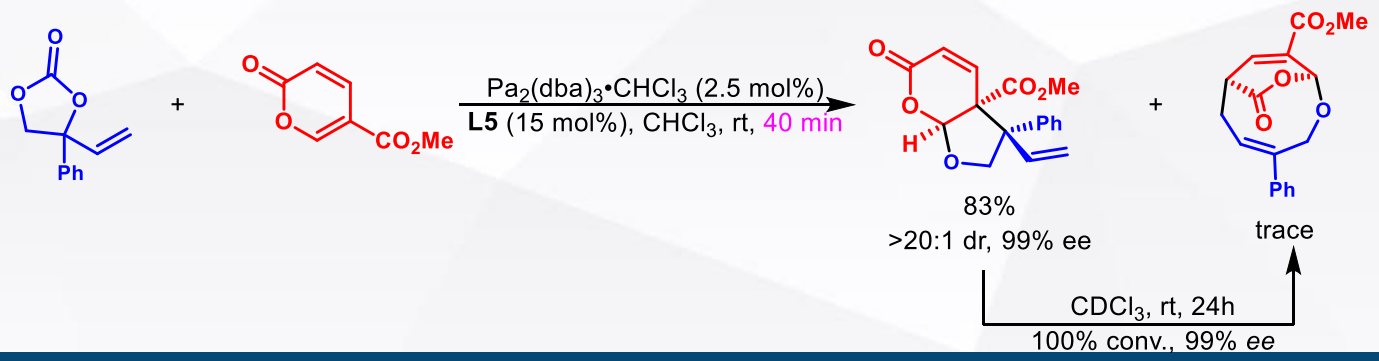


2.1 *C,O*-偶极子

可能的机理：

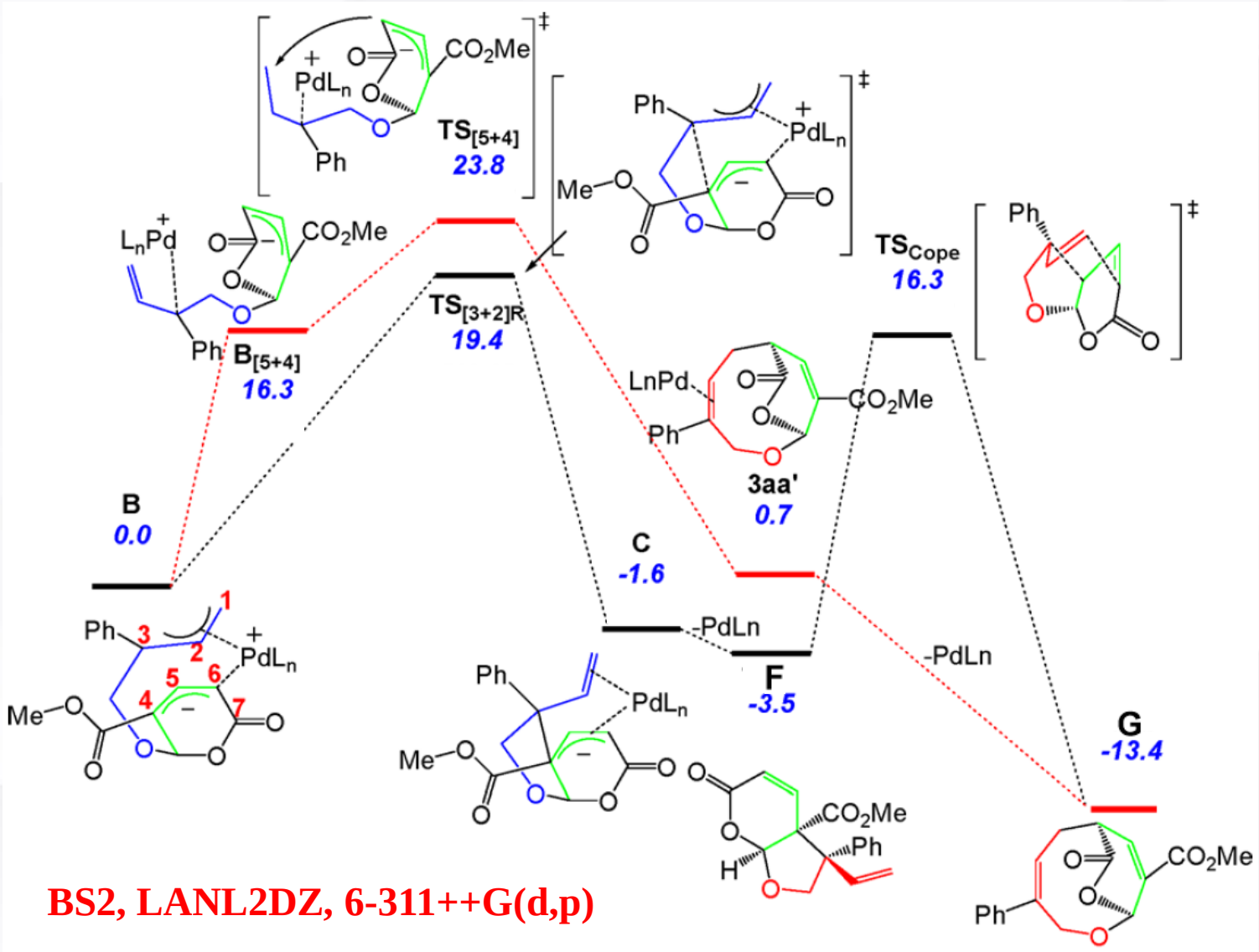


控制实验：



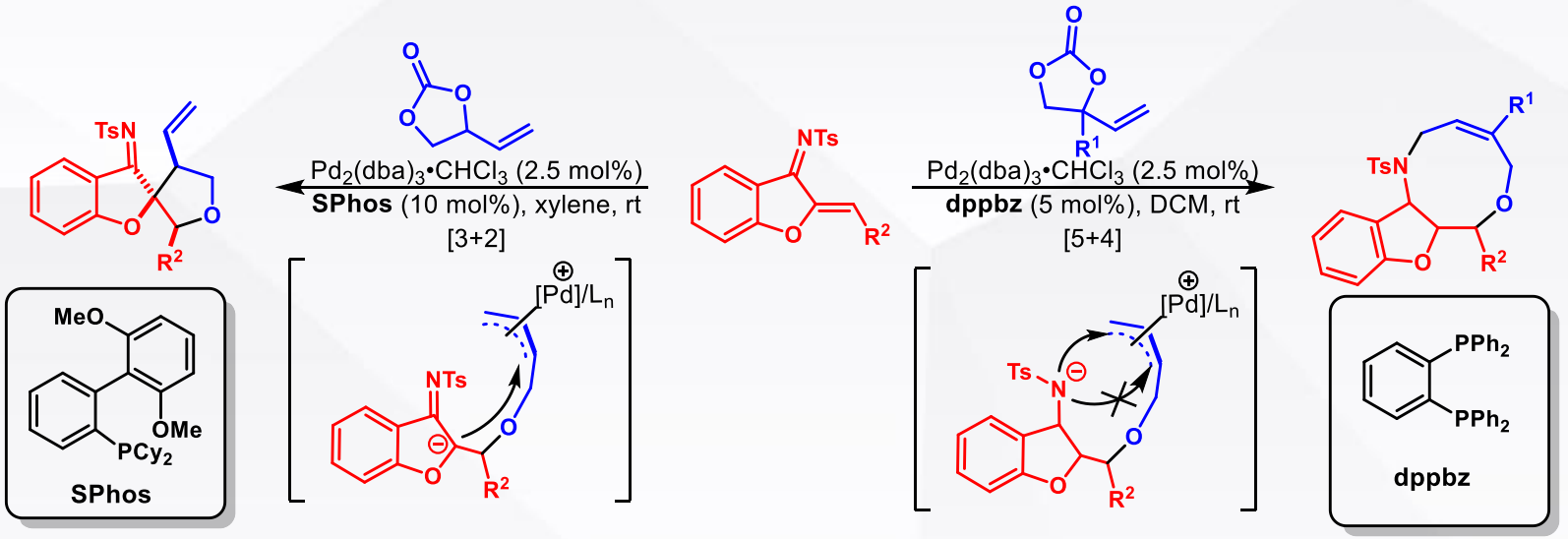
2.1 *C,O*-偶极子

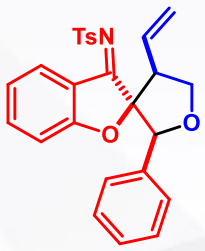
吉布斯自由能曲线：



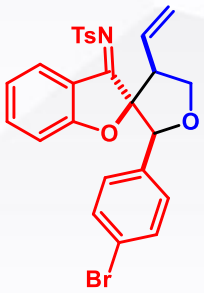
2.1 *C,O*-偶极子

配体控制的[3+2]环加成：

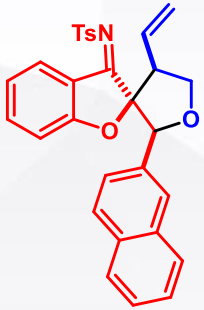




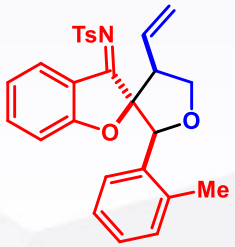
75% yield,
12:1 *dr*



76% yield,
19:1 *dr*



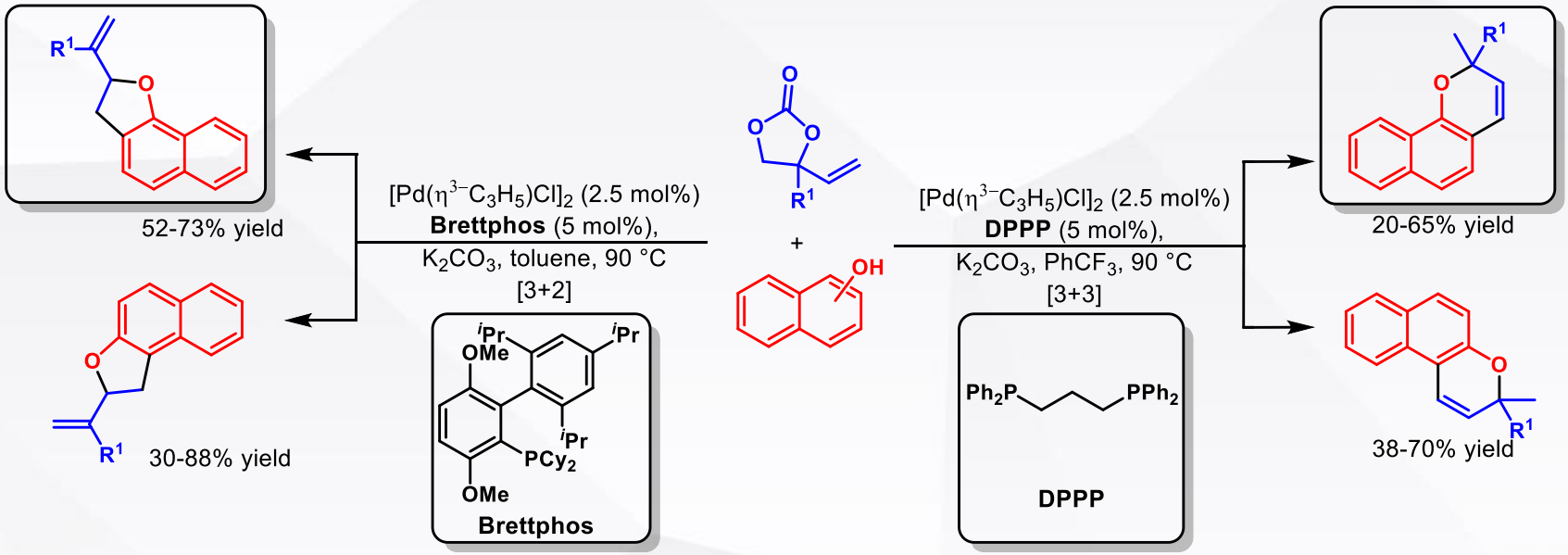
51% yield,
8:1 *dr*

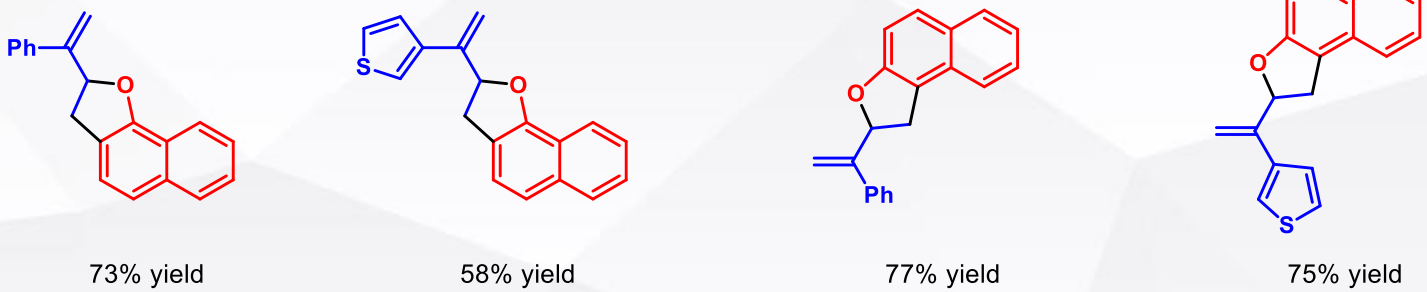


75% yield,
12:1 *dr*

2.1 *C,O*-偶极子

配体控制的[3+2]环加成：

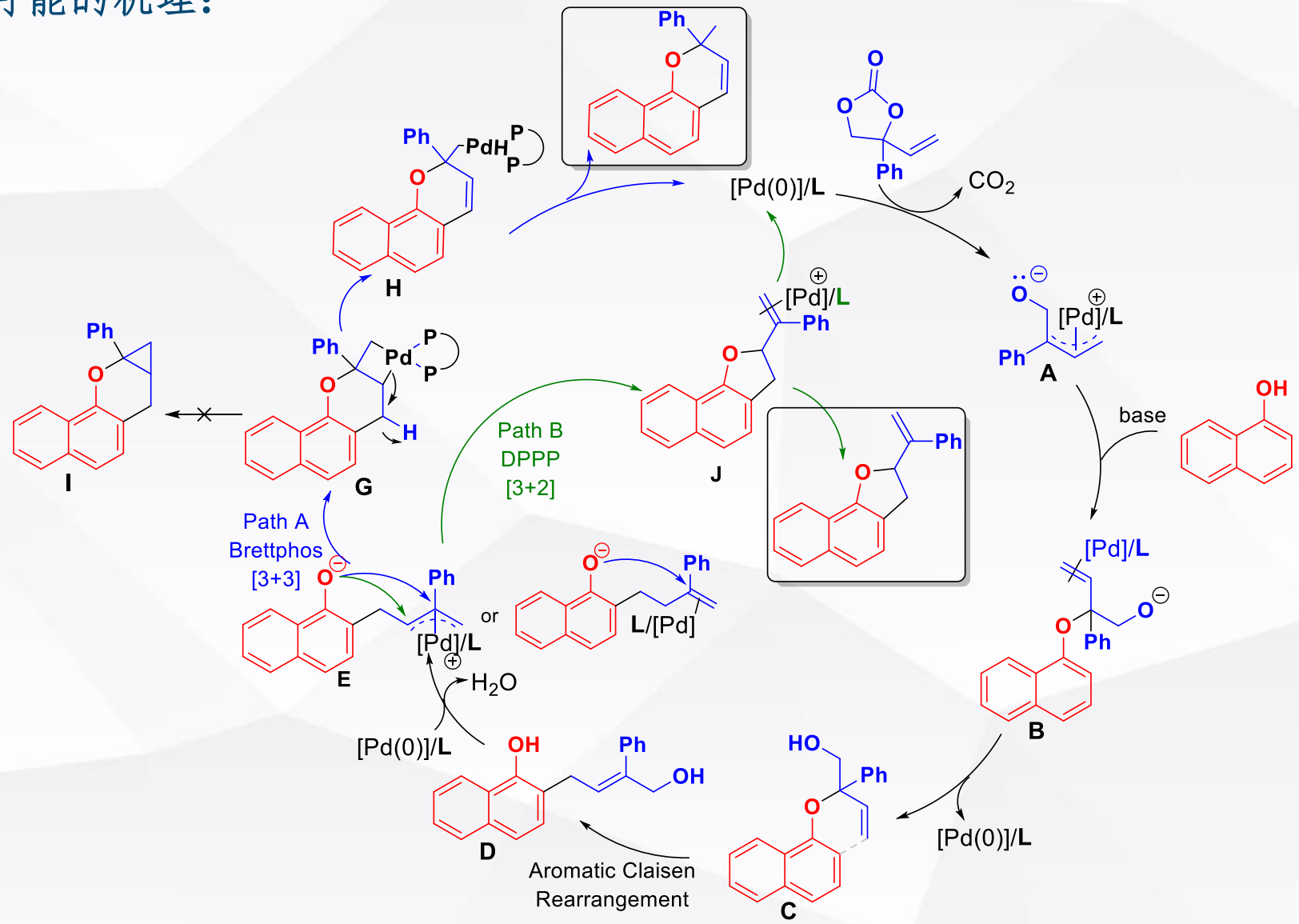




Y. M. Liang, *Chem. Commun.* **2019**, *55*, 4675-4678.

2.1 *C,O*-偶极子

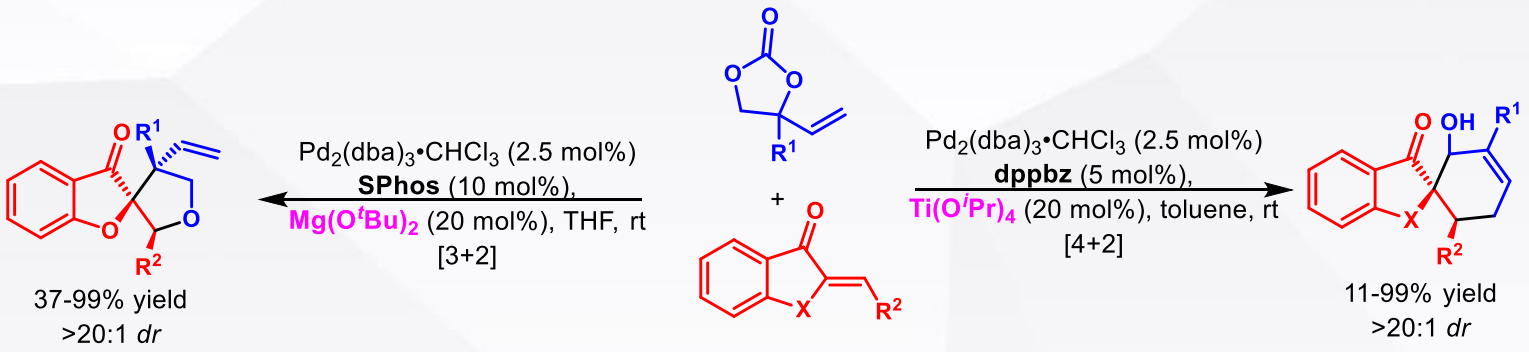
可能的机理：

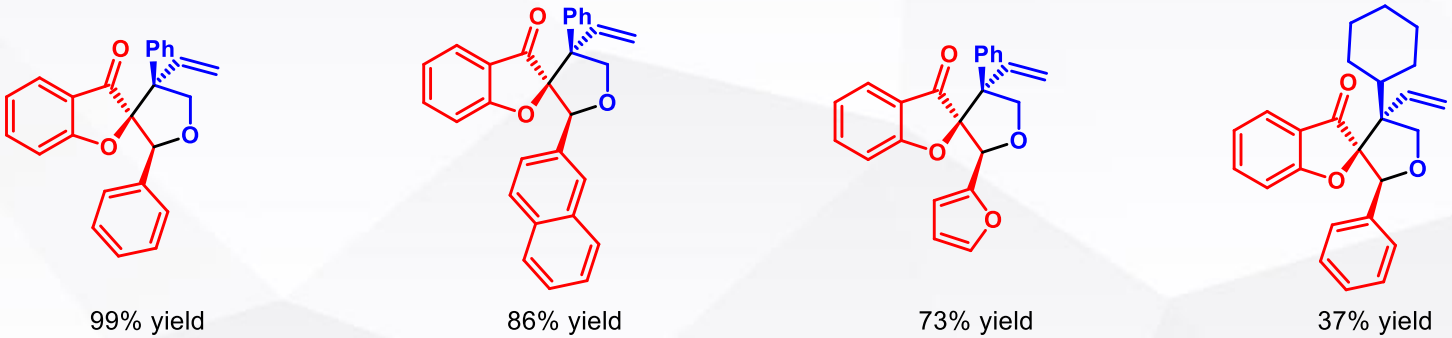


Y. M. Liang, *Chem. Commun.* **2019**, *55*, 4675-4678.

2.1 *C,O*-偶极子

钯/路易斯酸双金属协同催化：

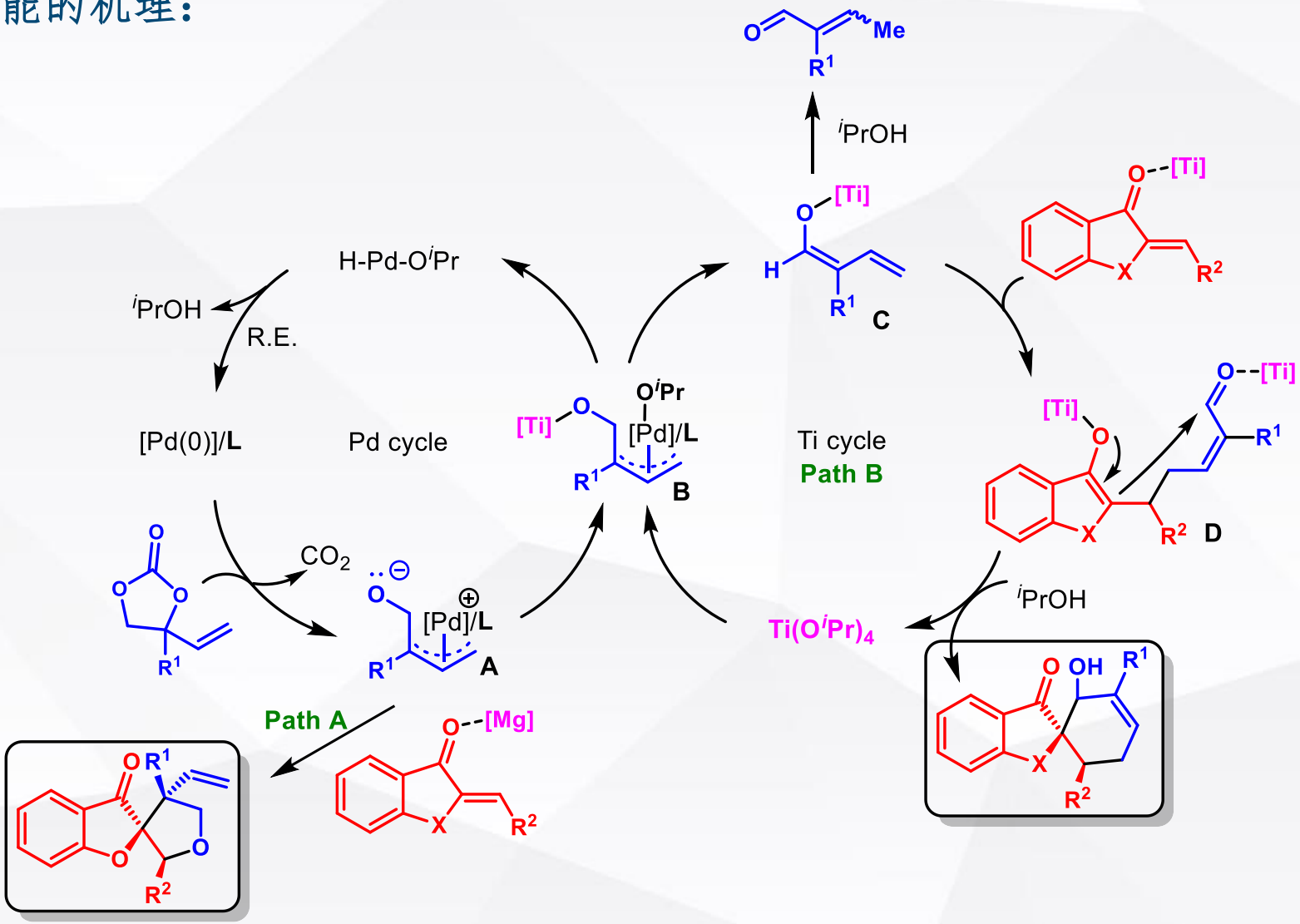




Y. Zhao, *Angew. Chem. Int. Ed.* **2018**, *57*, 7860-7864.

2.1 *C,O*-偶极子

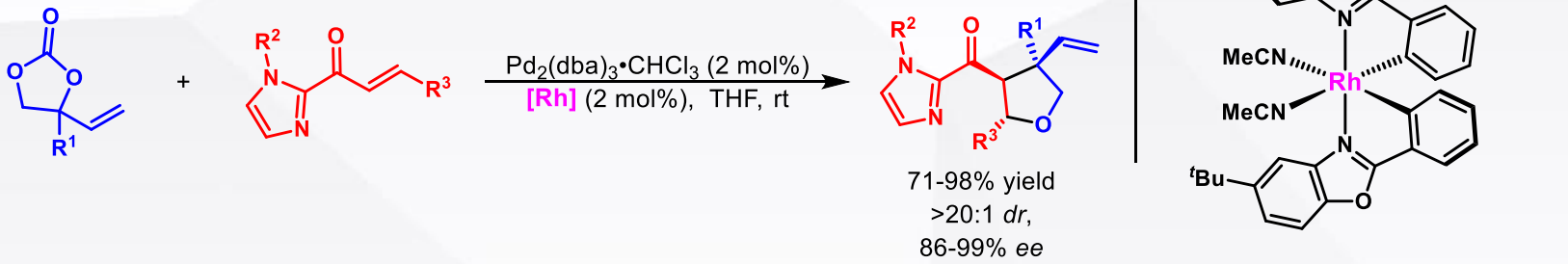
可能的机理：

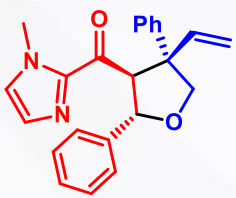


Y. Zhao, *Angew. Chem. Int. Ed.* **2018**, *57*, 7860-7864.

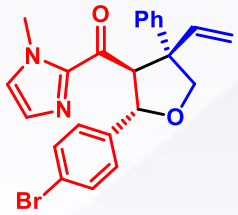
2.1 *C,O*-偶极子

钯/路易斯酸双金属协同催化：

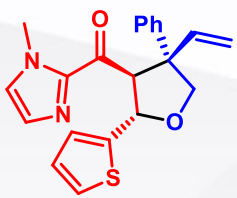




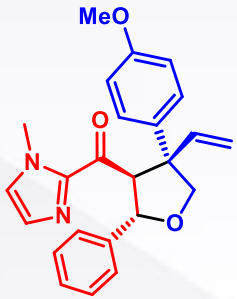
88% yield
>20:1 *dr*, 98% *ee*



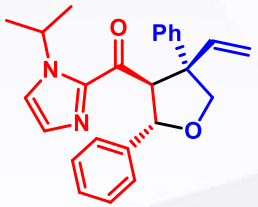
71% yield
>20:1 *dr*, 89% *ee*



78% yield
>20:1 *dr*, 86% *ee*



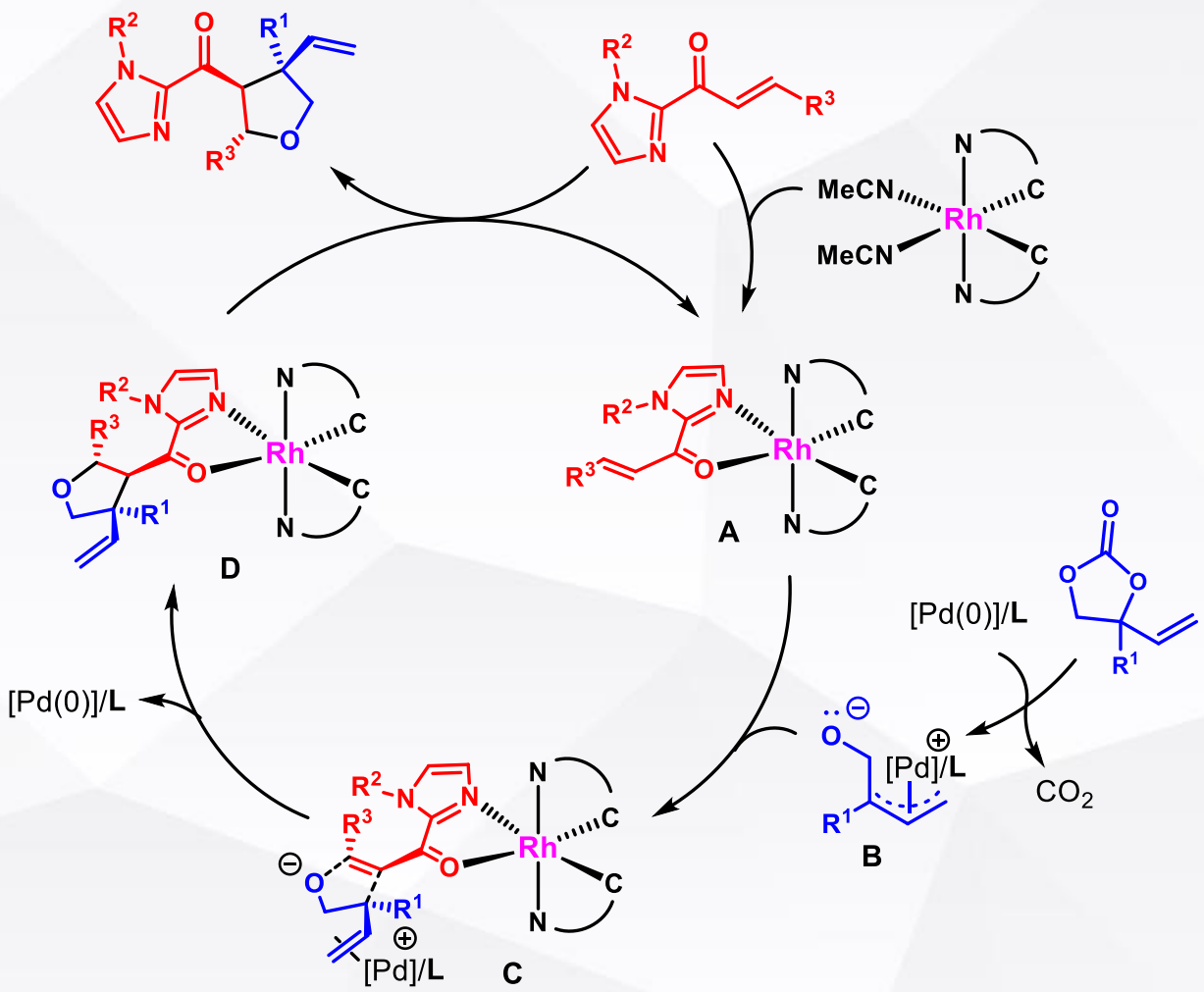
67% yield
>20:1 *dr*, 99% *ee*



81% yield
>20:1 *dr*, 96% *ee*

2.1 *C,O*-偶极子

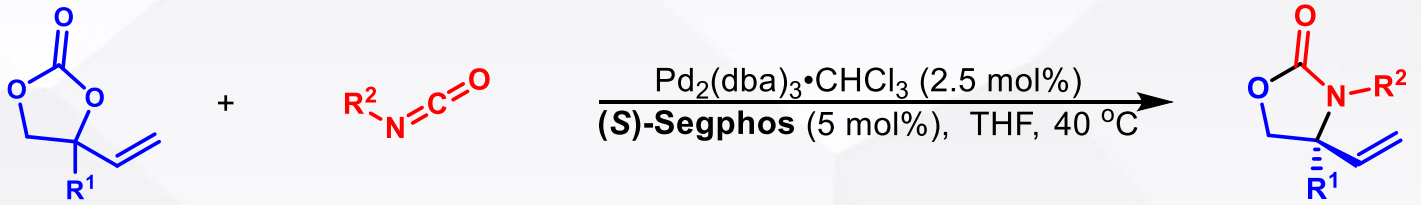
可能的机理：



2.1 *C,O*-偶极子

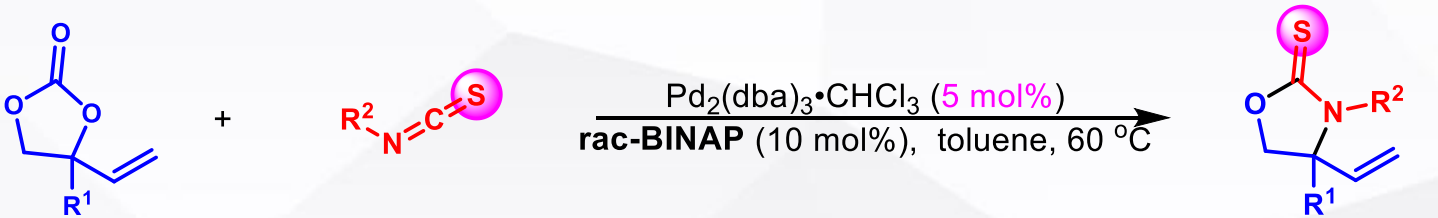
其他种类的不饱和双键：

异氰酸酯：



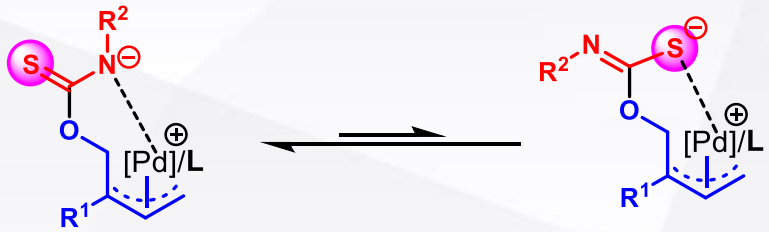
61-95% yield
37-99% *ee*

异硫氰酸酯：



up to 94% yield

C-N Formation

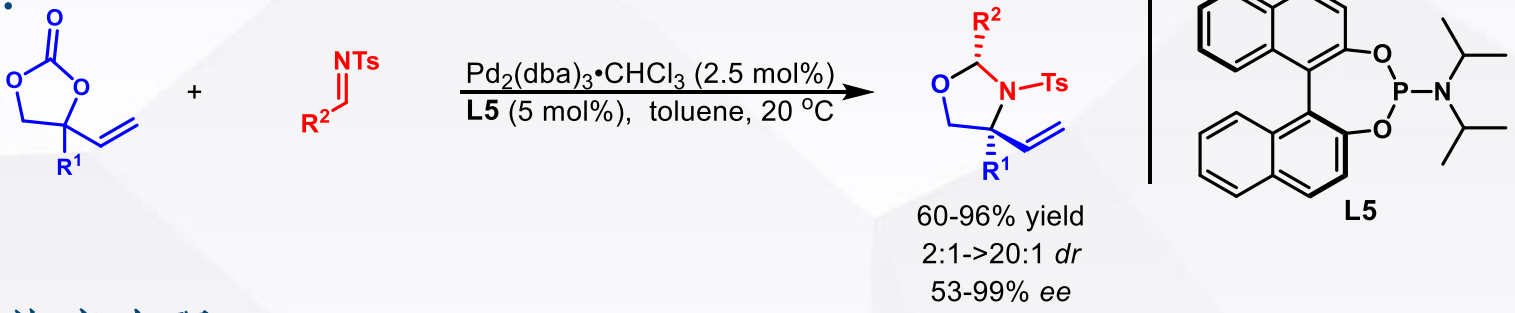


Y. J. Zhang, *Chem. Eur. J.* **2015**, *21*, 120-124. T. Y. Xu, *J. Org. Chem.* **2020**, *85*, 8773-8779.

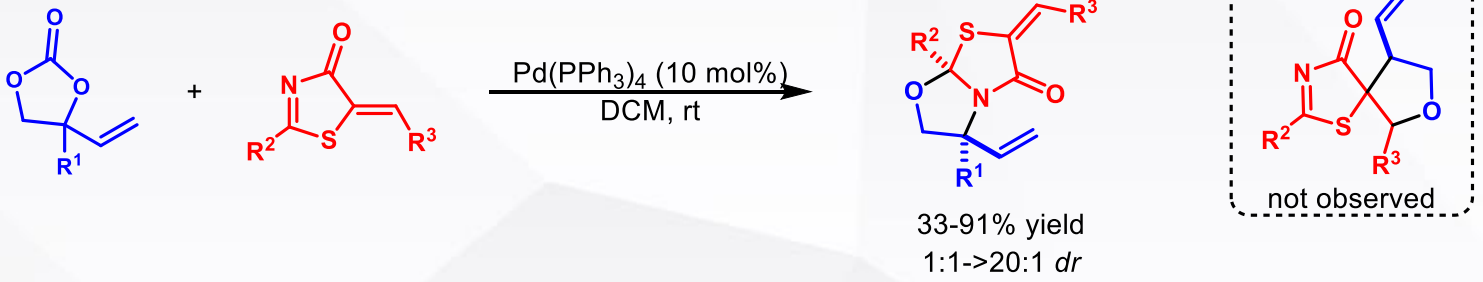
2.1 *C,O*-偶极子

其他种类的不饱和双键：

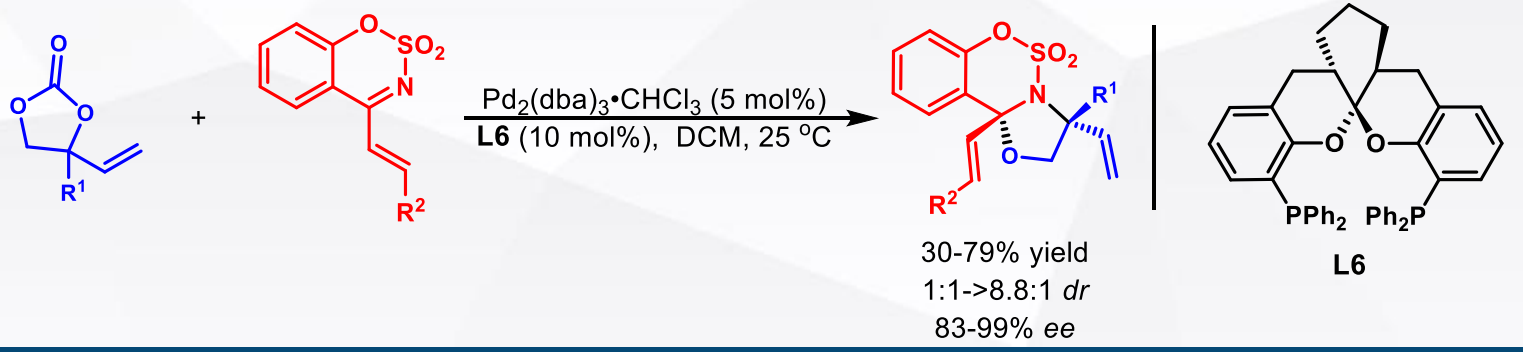
亚胺：



5-烯基噻唑酮：



环状N-磺酰基酮亚胺：



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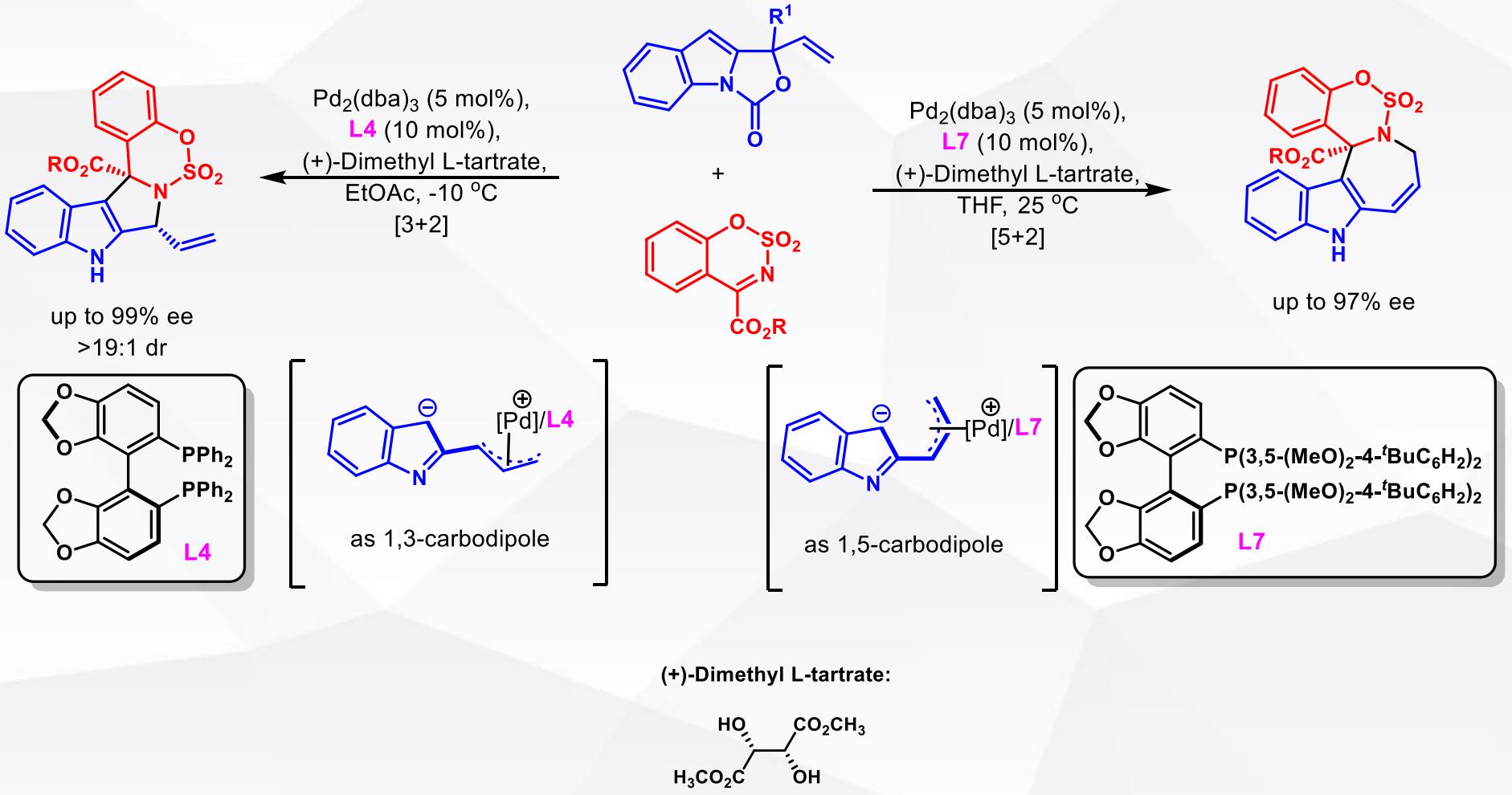
2.2 *C,C*-偶极子

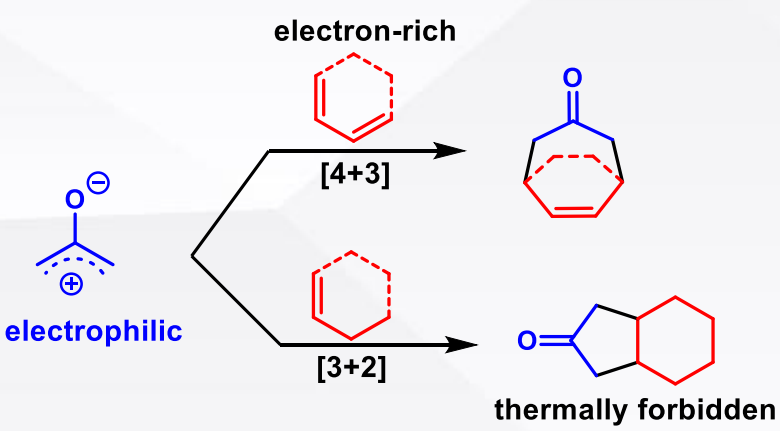
配体控制的[3+2]环加成：

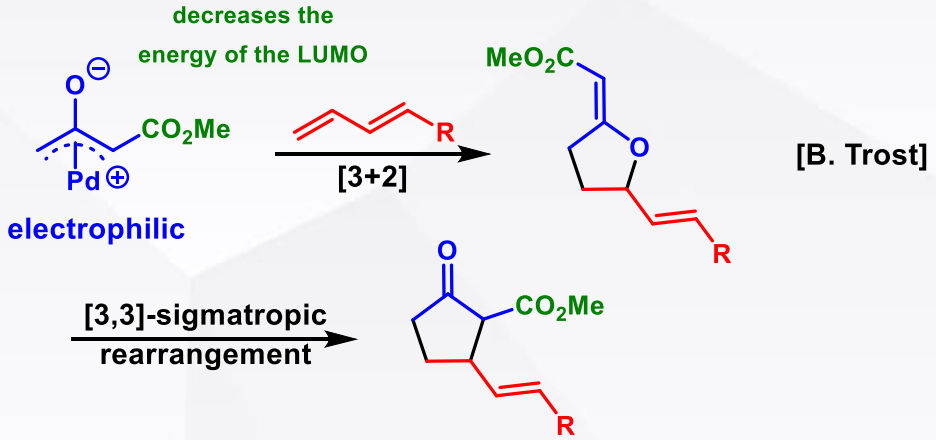


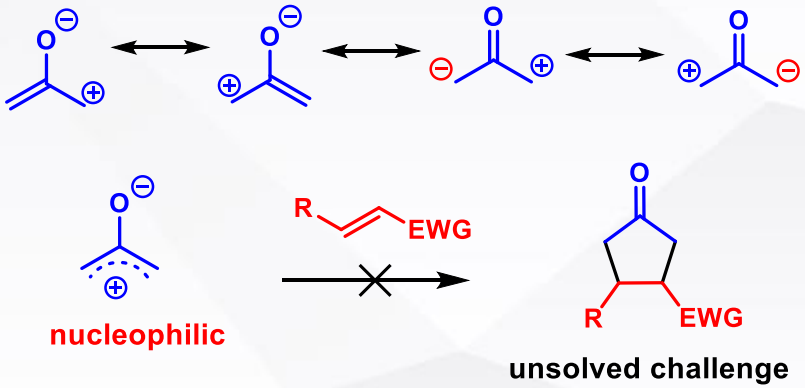
Y. C. Chen, *Org. Lett.* **2021**, *23*, 4791-4795.

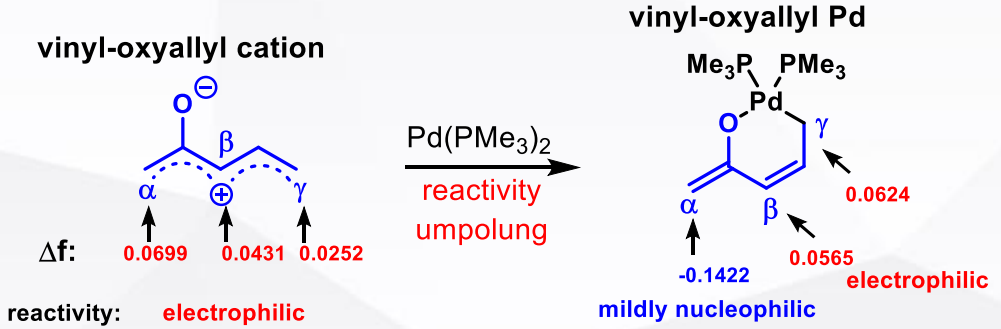
2.2 *C,C*-偶极子

反向电子需求：

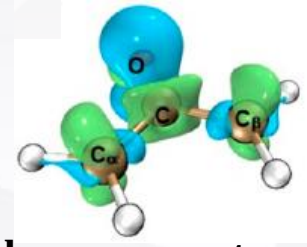


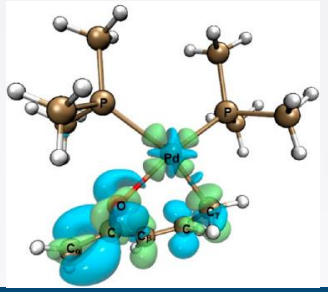






DFT calculations of the condensed dual descriptor

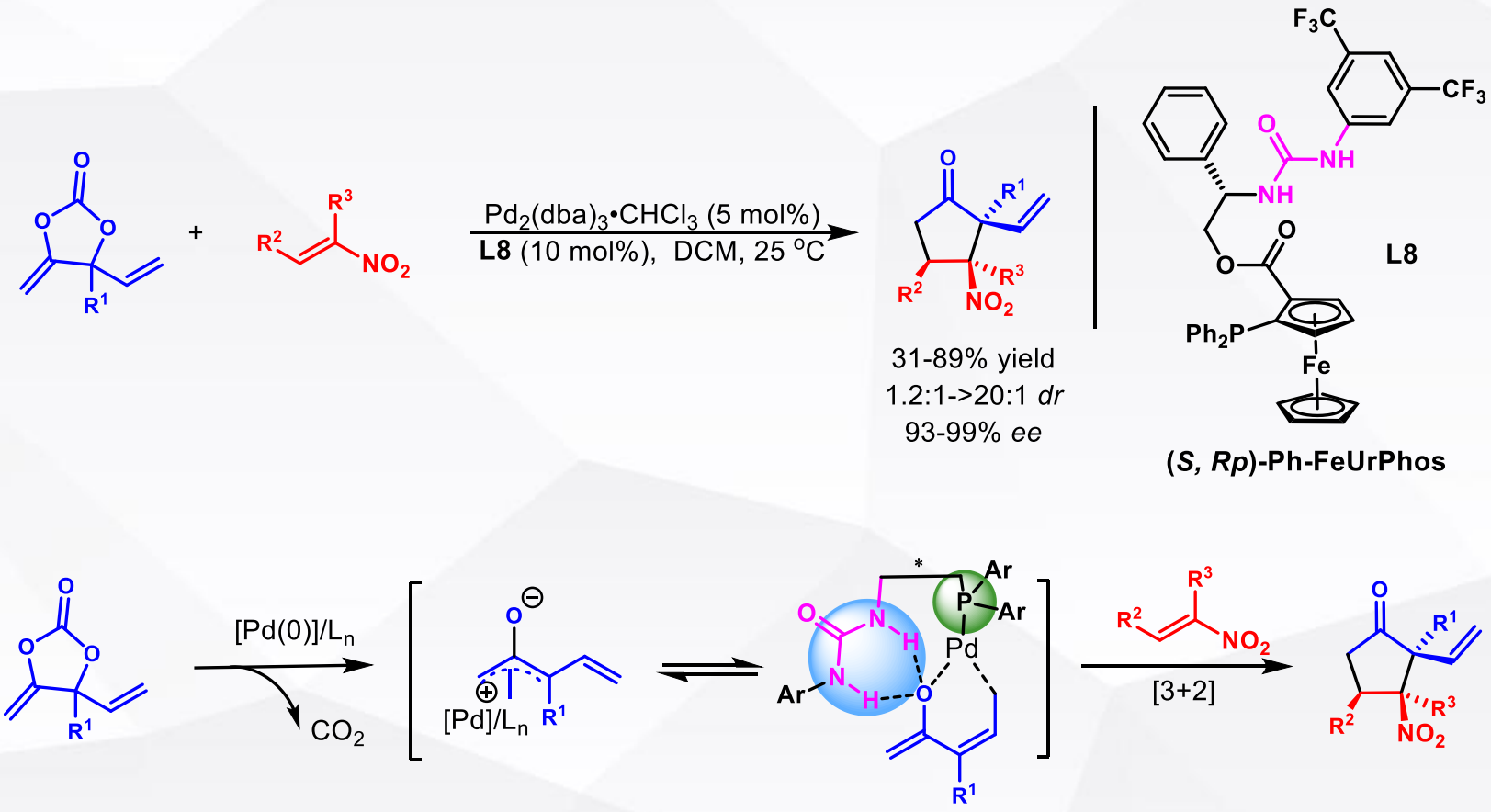




Topology of dual descriptor isosurfaces:
Green lobes represent electrophilicity, and blue lobes represent nucleophilicity

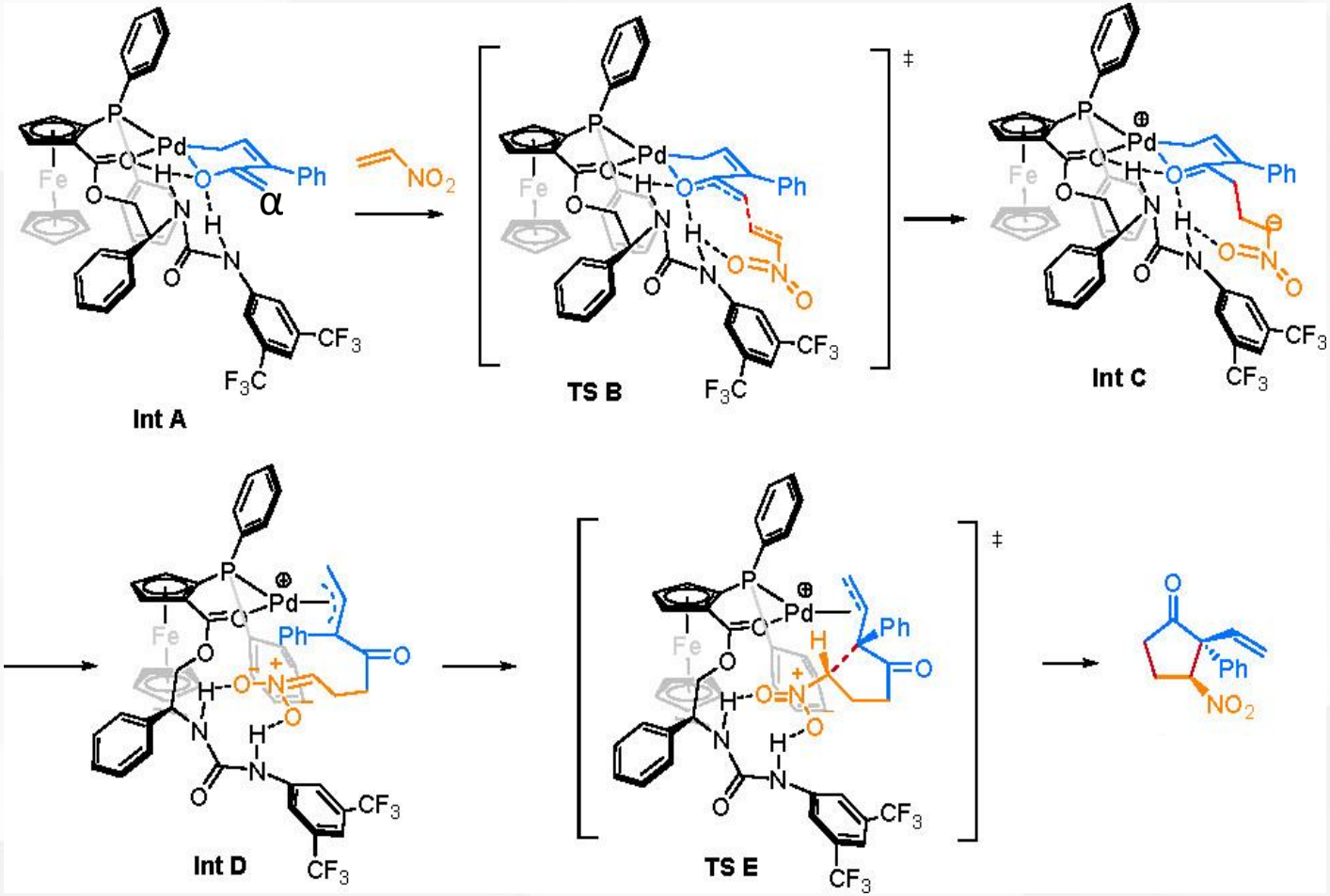
2.2 *C,C*-偶极子

反向电子需求：



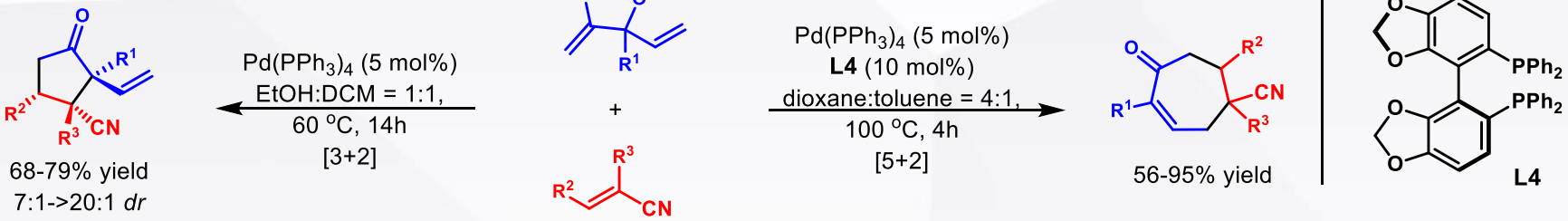
2.2 *C,C*-偶极子

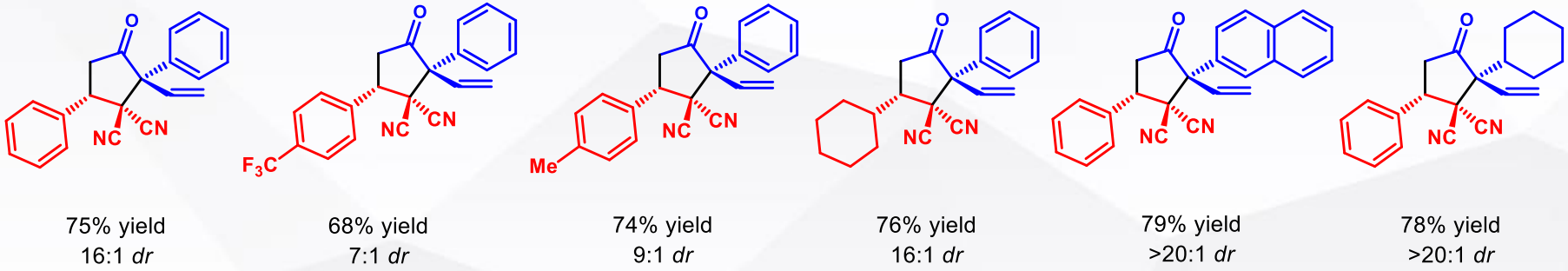
可能的机理：



2.2 *C,C*-偶极子

反向电子需求：





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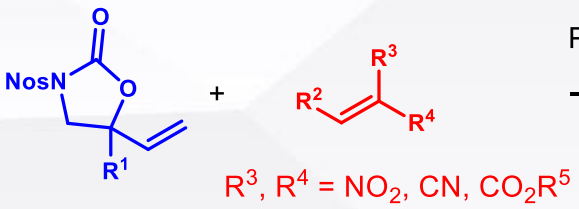
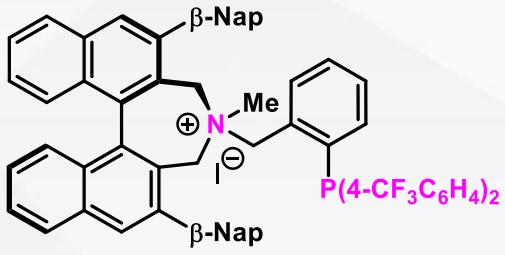
2.3 *C,N*-偶极子

缺电子烯烃：

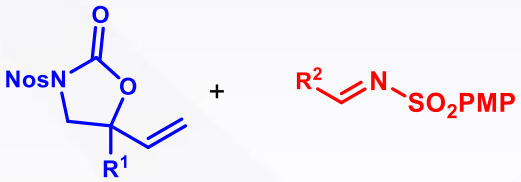


70-99% yield
8.6:1->20:1 *dr*
93-99% *ee*

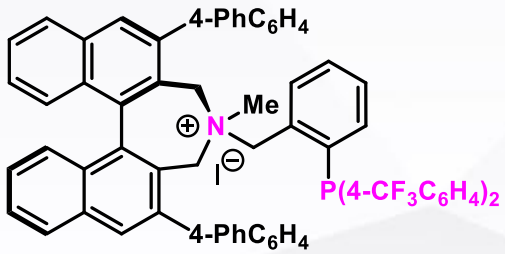


L9

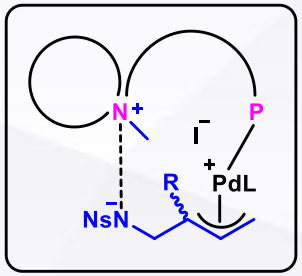
亚胺：



80-99% yield
6:1->20:1 *dr*
92-98% *ee*



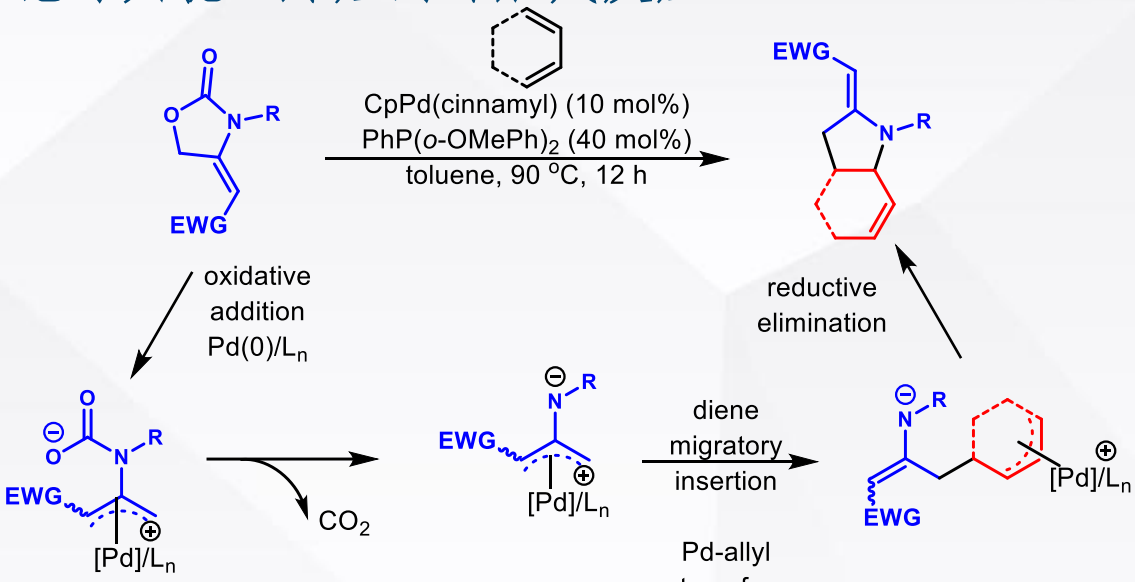
L10

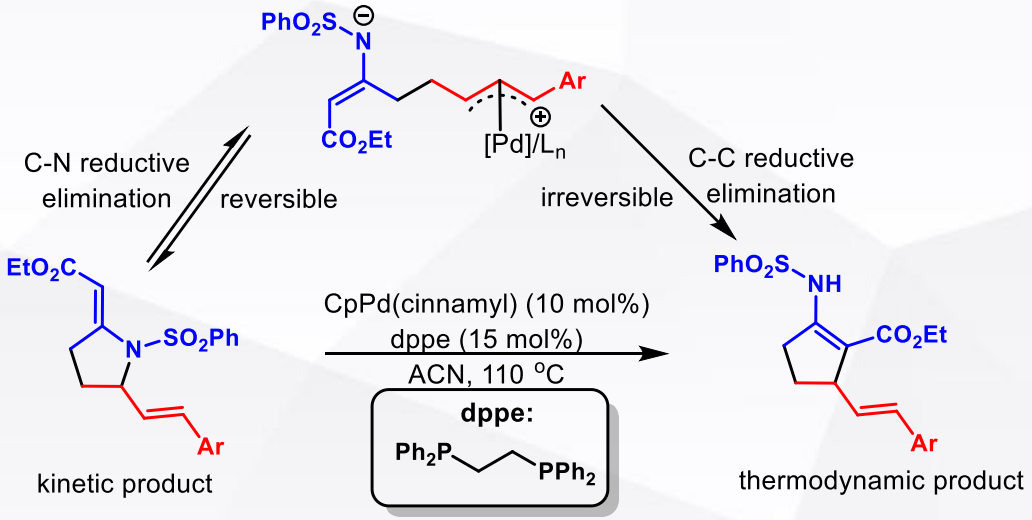


双离子对作用

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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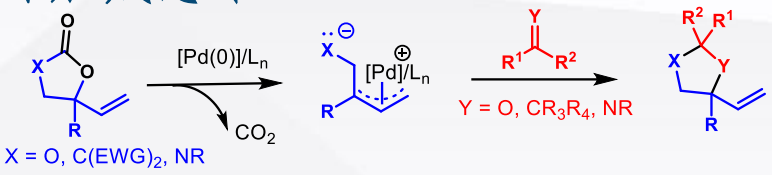
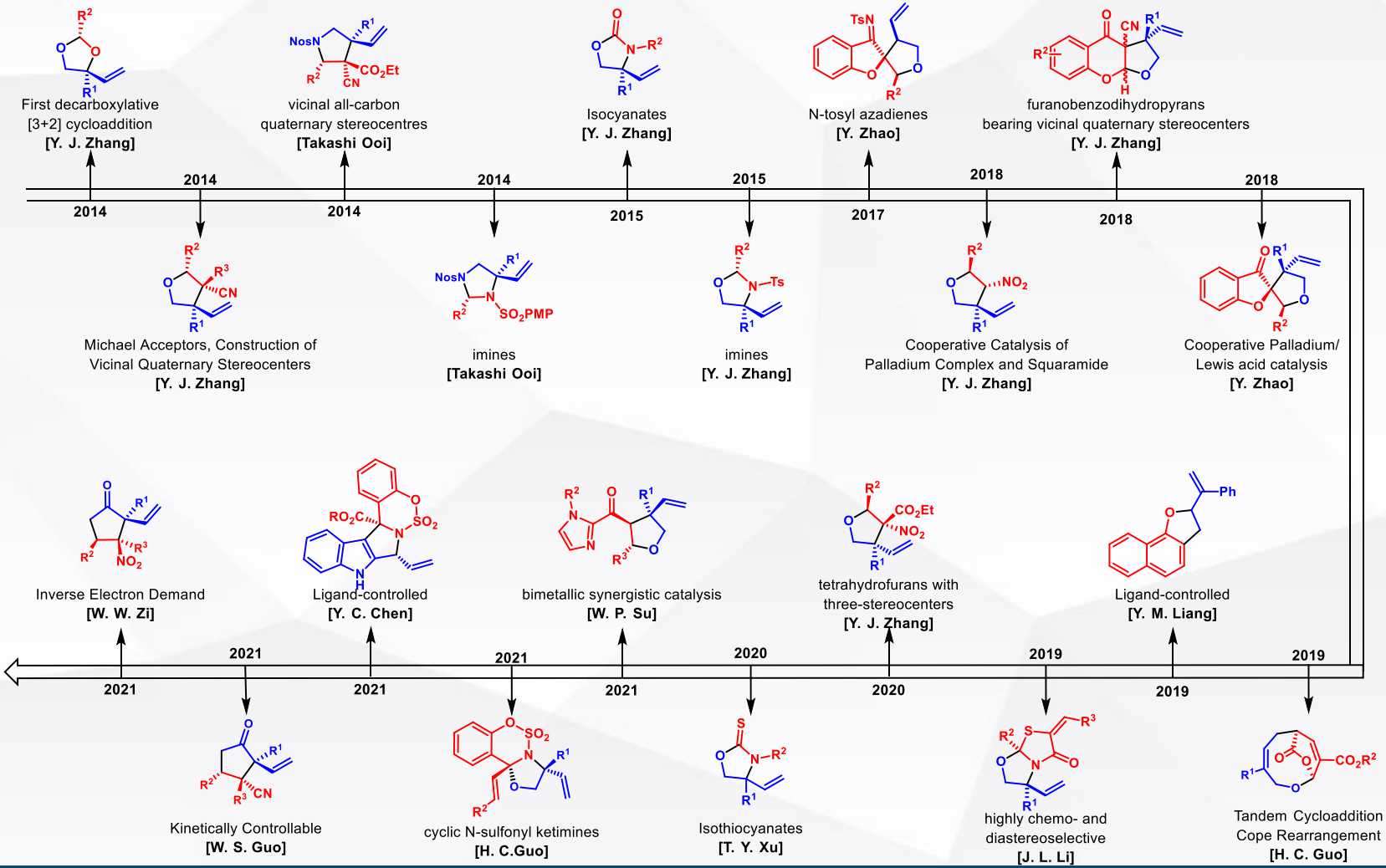
3. 总结与展望

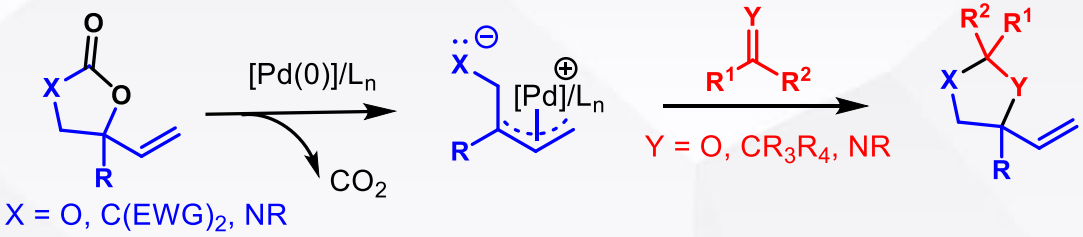
近年来钯催化脱酸[3+2]环加成总结：



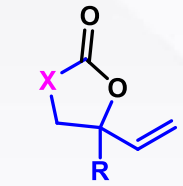


3. 总结与展望

展望：

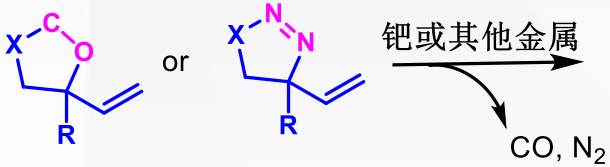


1.

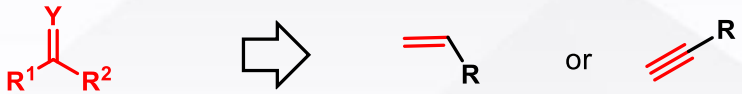


X = S, Si(EWG)$_2$, PR, P(O)R$_2$

2.



3.



Y = O, CR$_3$R$_4$, NR

很少报道

谢谢