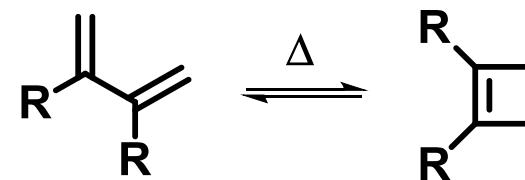


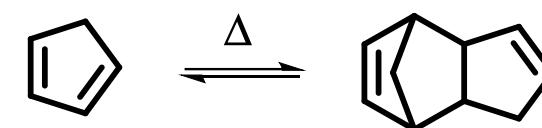
Cycloisomerization and cyclization reactions

➤ Transition-metal-free cycloisomerization and cyclization reactions

- cycloisomerization

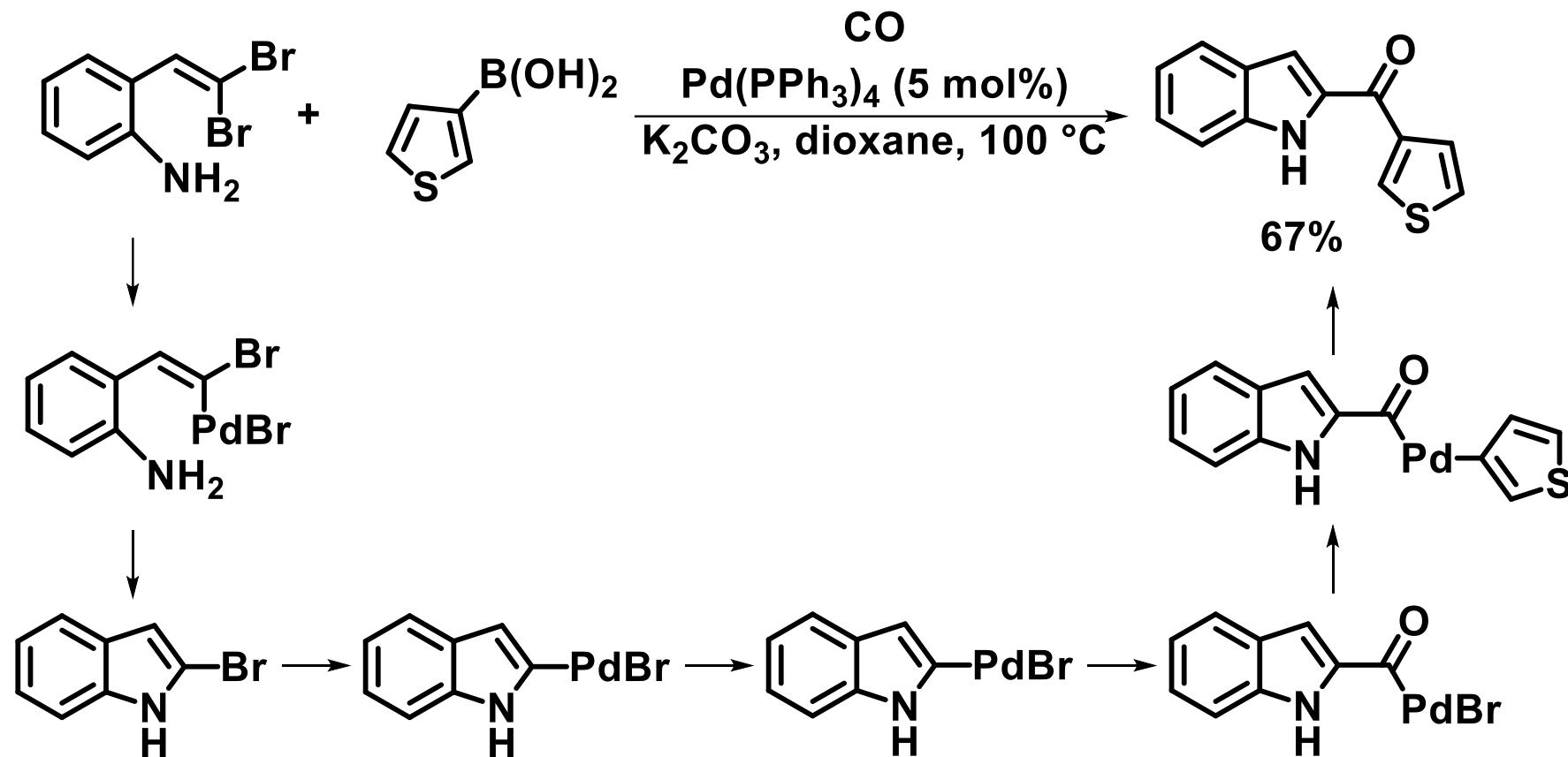


- cyclization



Cycloisomerization and cyclization reactions

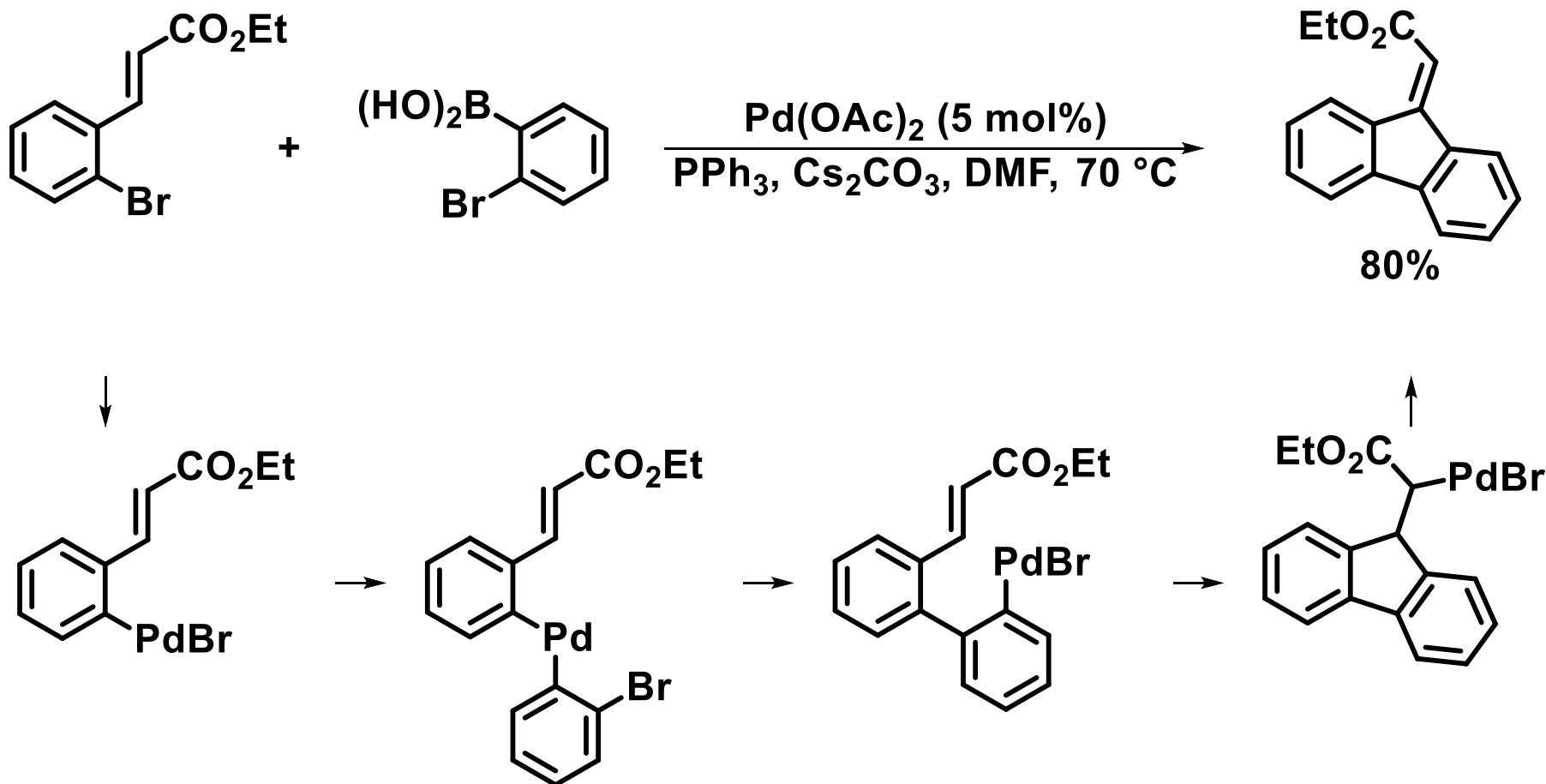
➤ Transition-metal-catalyzed cyclization reactions:
Intramolecular version of cross-coupling reactions



Org. Lett. 2009, 11, 4608

Cycloisomerization and cyclization reactions

- Transition-metal-catalyzed cyclization reactions:
Intramolecular version of cross-coupling reactions

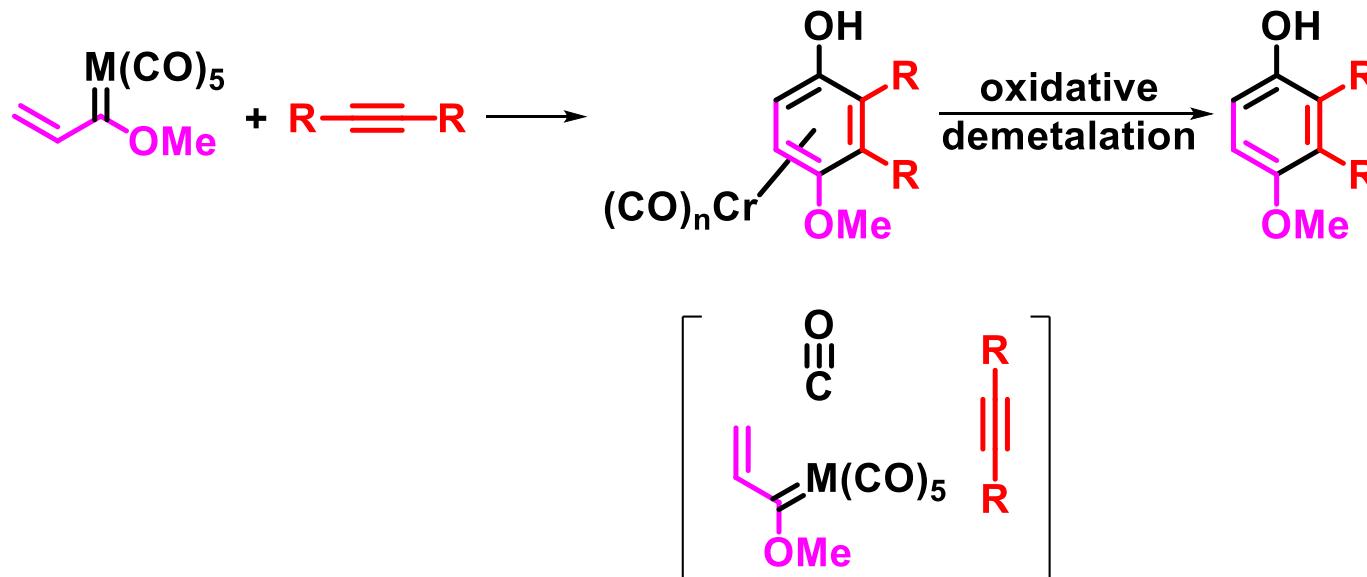


Tetrahedron Lett. **2011**, *52*, 4051

Cycloisomerization and cyclization reactions

➤ Fischer carbene complexes

- Reactivity of Fischer carbene complexes ($\text{C}=\text{Cr}(\text{CO})_5 \approx \text{C}=\text{O}$)
 - Reaction with alkynes – Dötz reaction



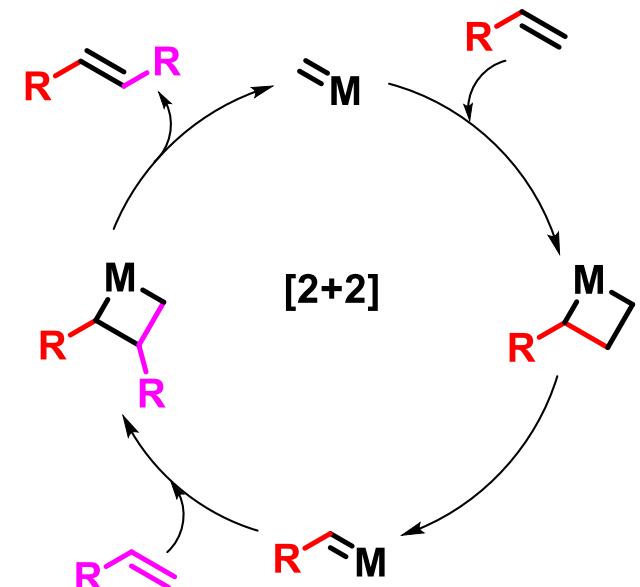
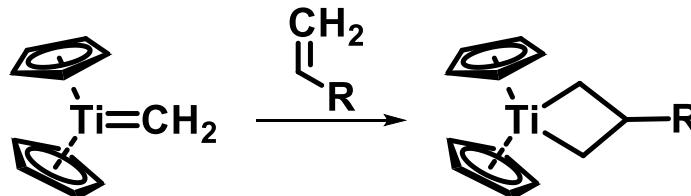
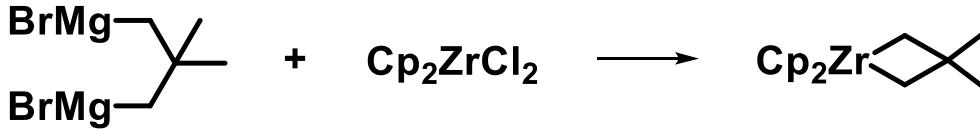
Cycloisomerization and cyclization reactions

➤ Metallacycles

- Metallacyclobutanes



- Preparation



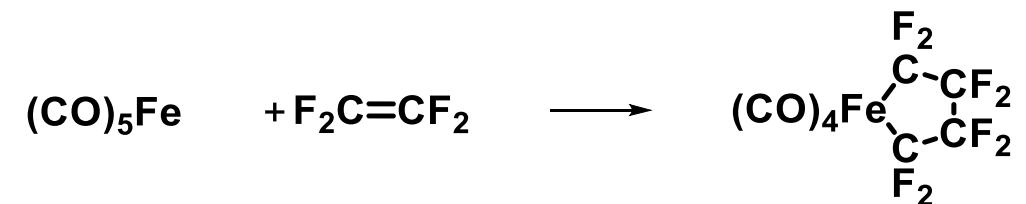
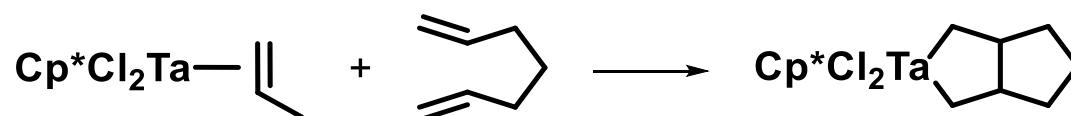
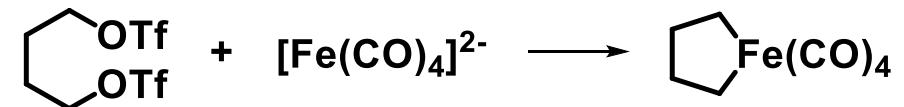
Cycloisomerization and cyclization reactions

➤ Metallacycles

- Metallacyclopentanes



- Preparation



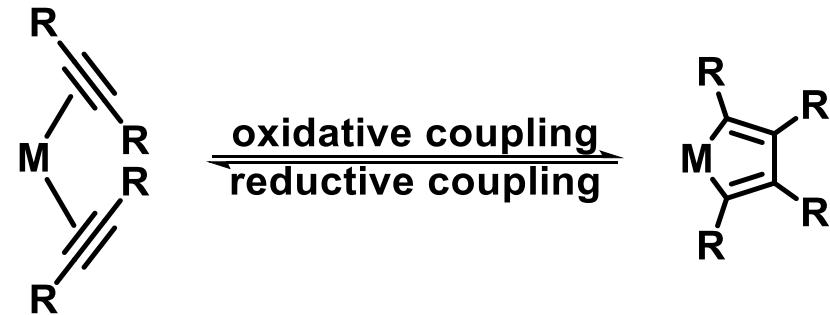
Cycloisomerization and cyclization reactions

➤ Metallacycles

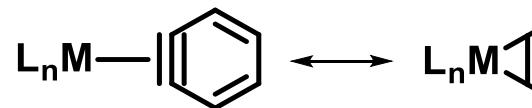
- Metallacyclopentadienes



- Preparation



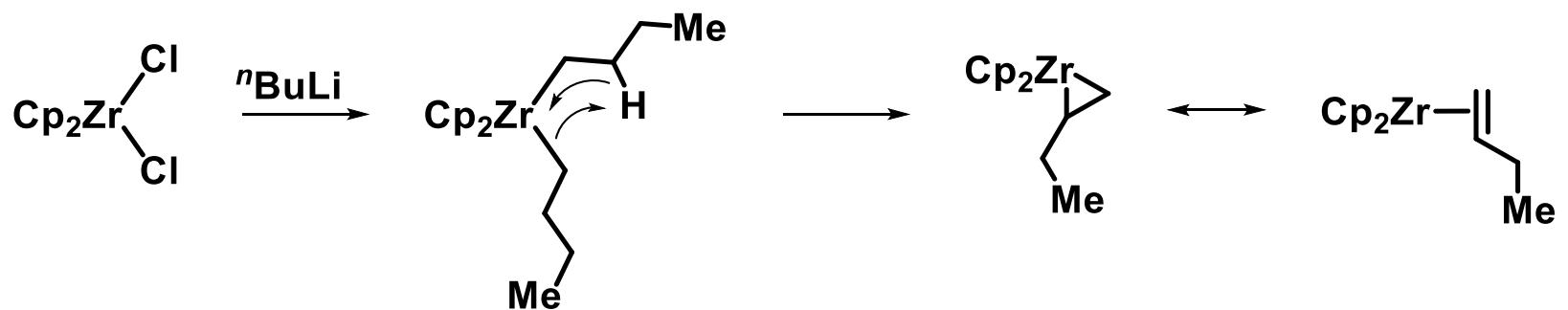
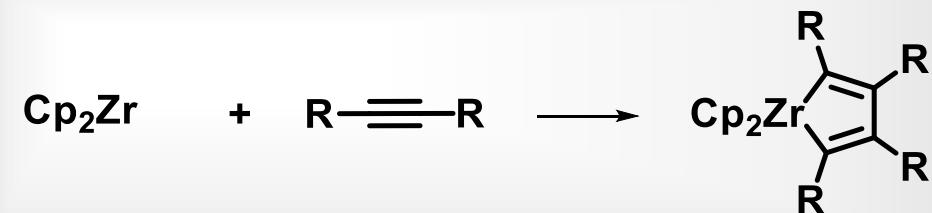
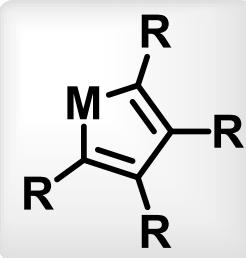
- Other metallacycles



Cycloisomerization and cyclization reactions

► Metallacycles

- Metallacyclopentadienes – Fagan-Nugent reaction

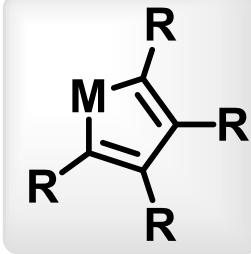
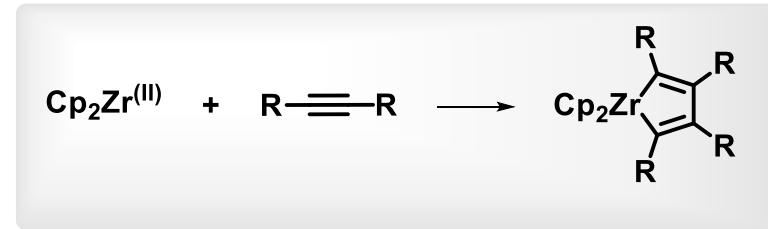


Acc. Chem. Res. **1994**, 27, 124

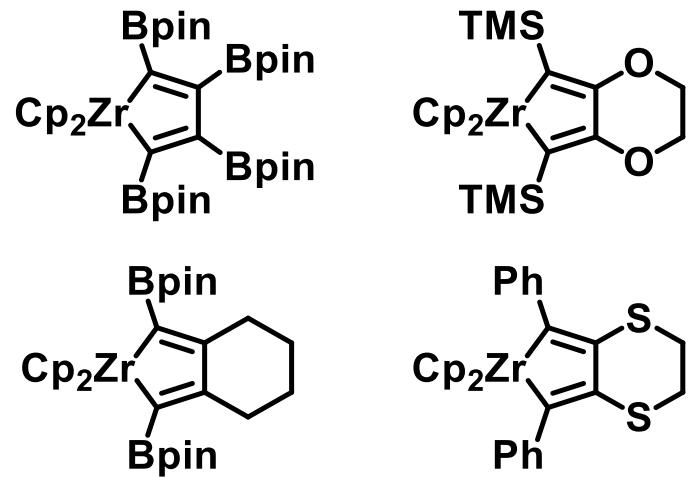
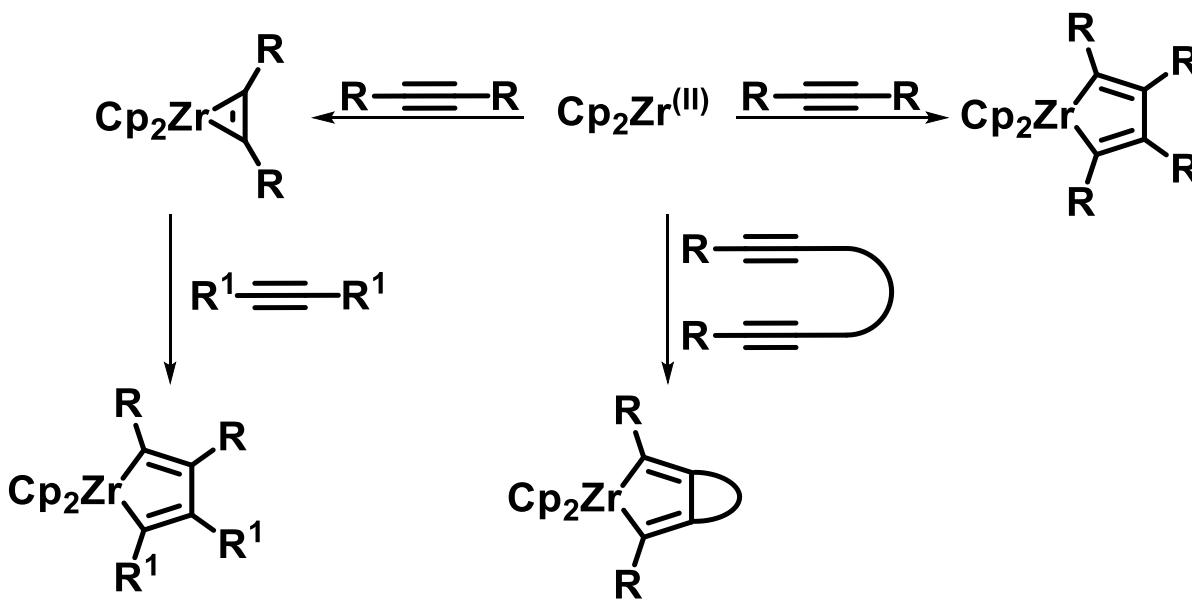
Cycloisomerization and cyclization reactions

► Metallacycles

- Metallacyclopentadienes – Fagan-Nugent reaction



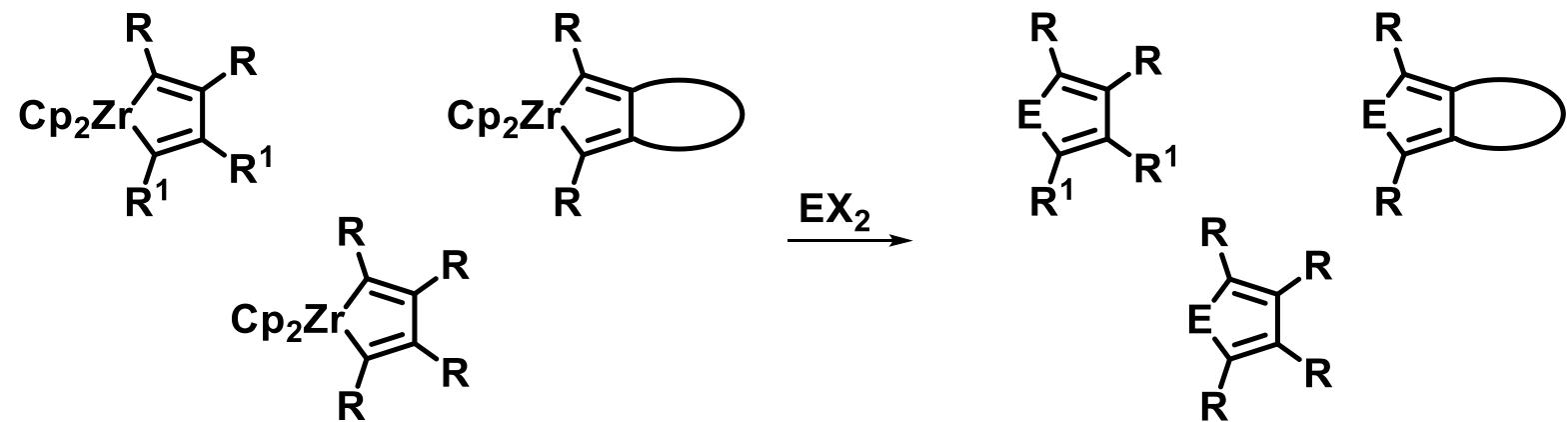
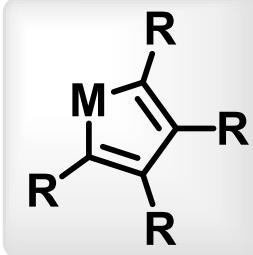
- Examples of prepared zirconacyclopentadienes



Cycloisomerization and cyclization reactions

► Metallacycles

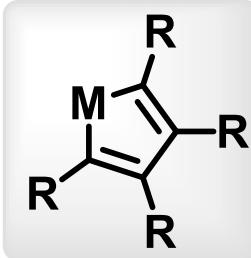
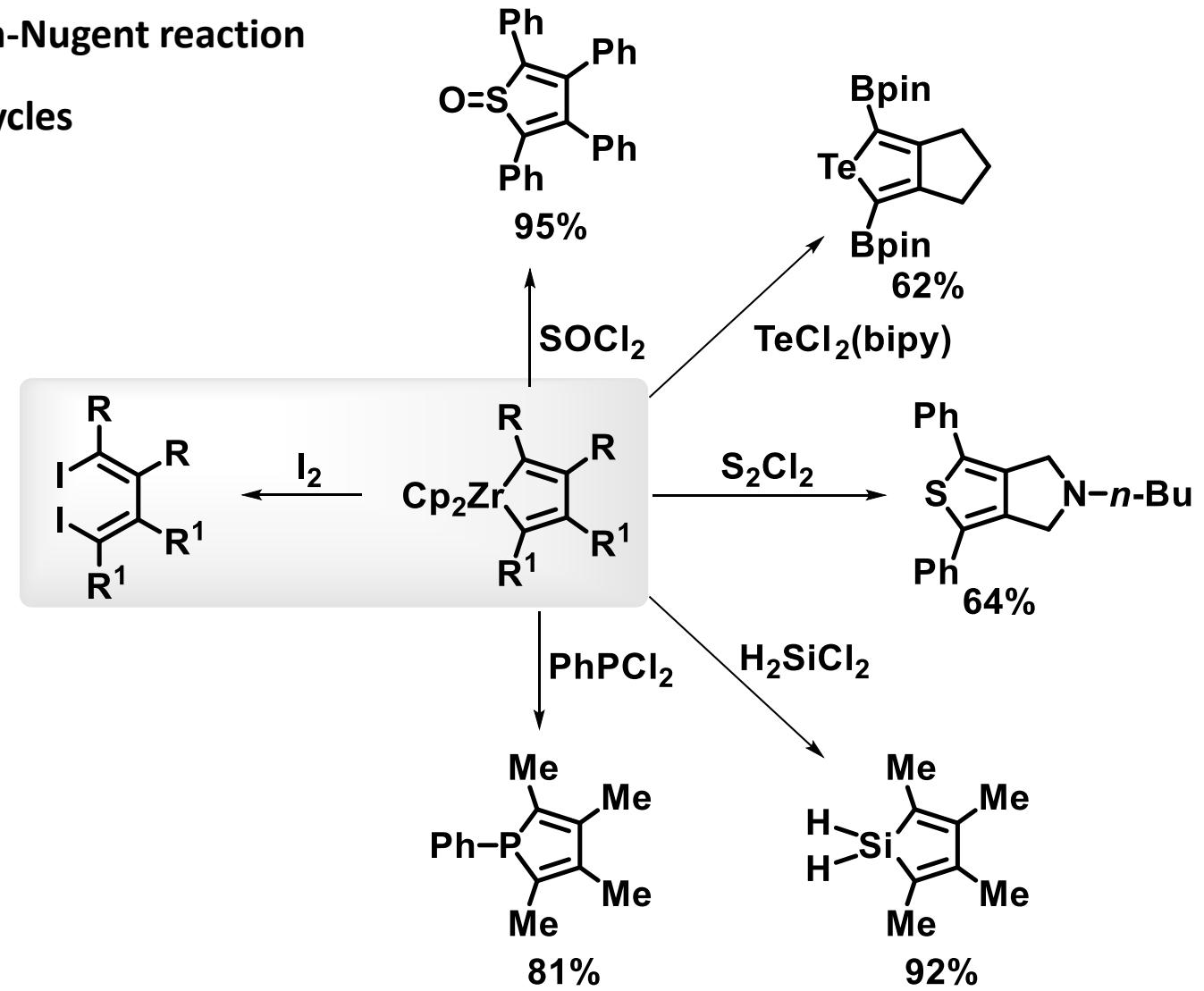
- Metallacyclopentadienes – Fagan-Nugent reaction
 - Synthesis of heterocycles



Cycloisomerization and cyclization reactions

➤ Metallacycles

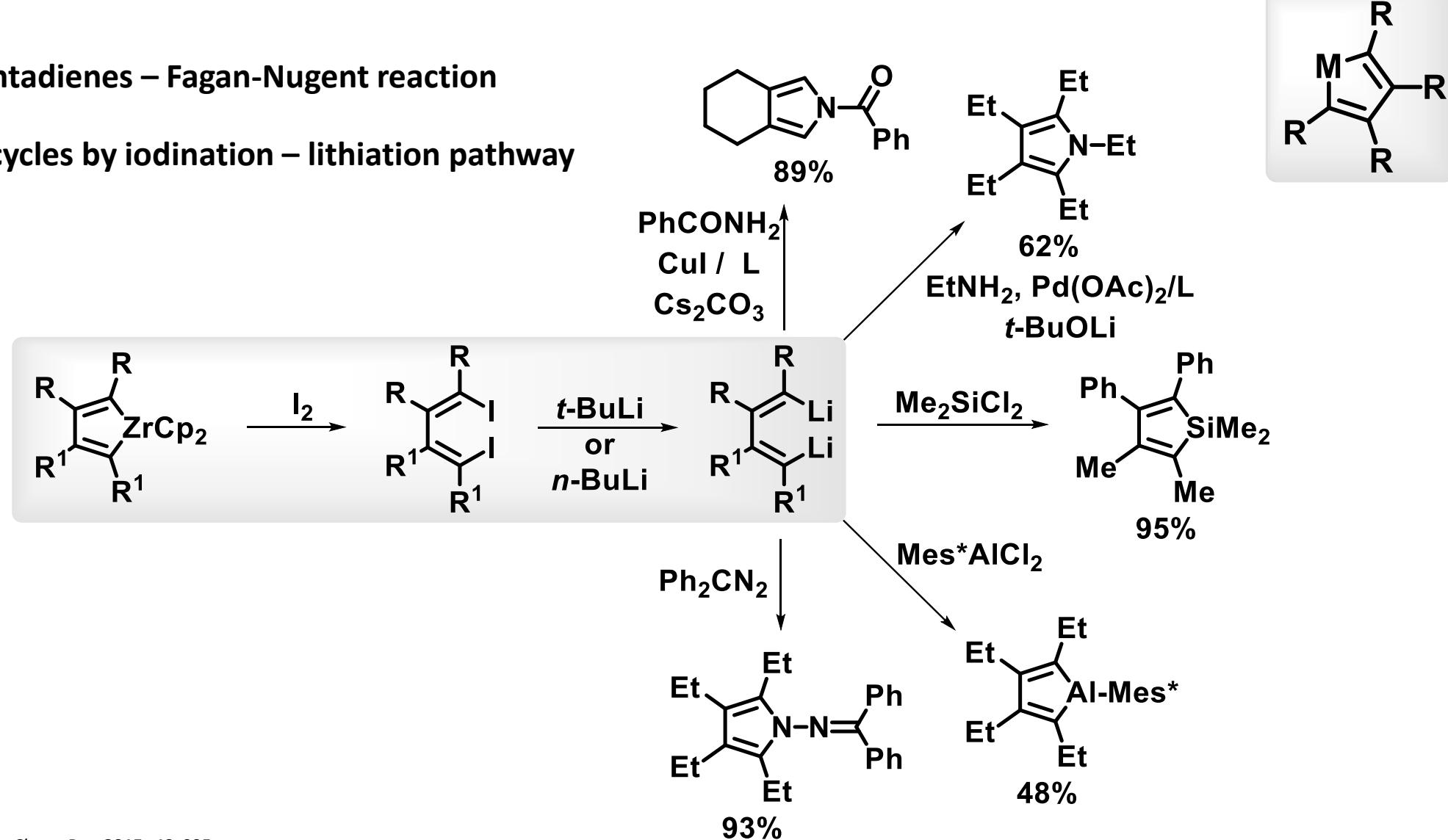
- Metallacyclopentadienes – Fagan-Nugent reaction
 - Direct synthesis of heterocycles



Cycloisomerization and cyclization reactions

► Metallacycles

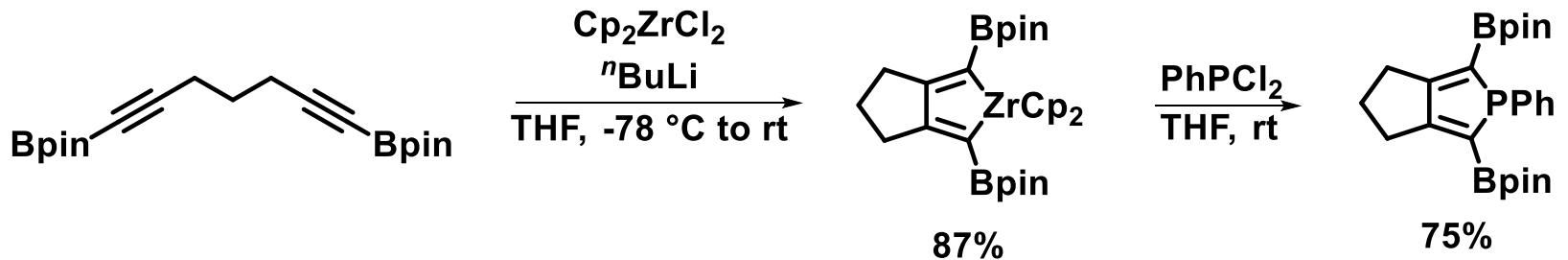
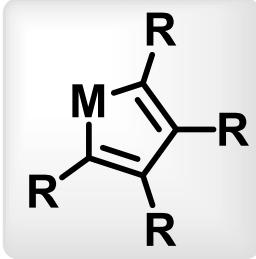
- Metallacyclopentadienes – Fagan-Nugent reaction
- Synthesis of heterocycles by iodination – lithiation pathway



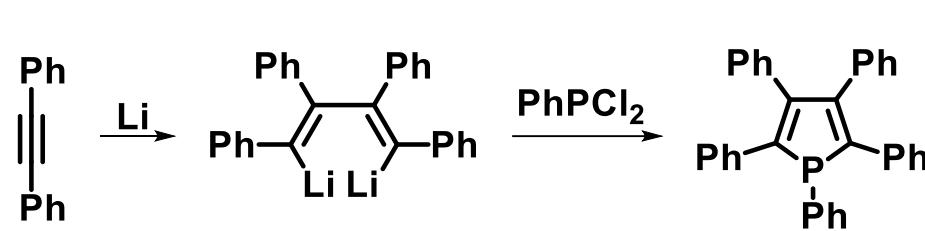
◦ For review see: *Acc. Chem. Res.* 2015, 48, 935

➤ Metallacycles

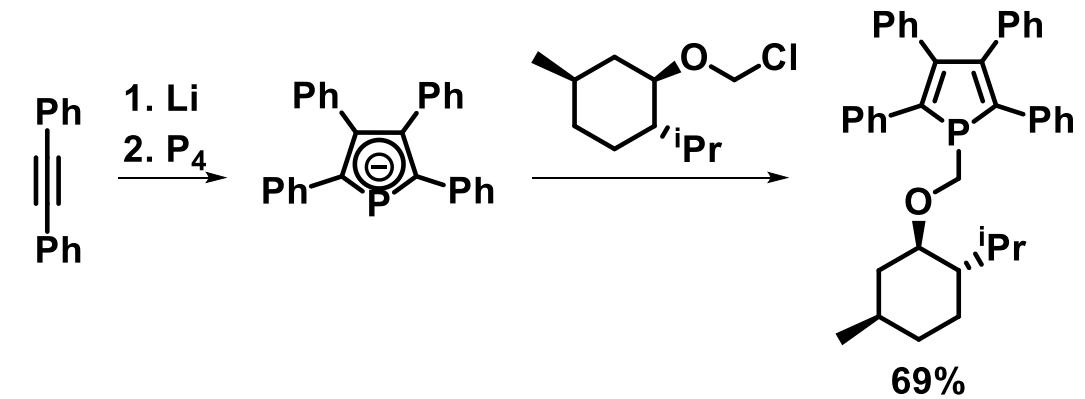
- Metallacyclopentadienes – Fagan-Nugent reaction
- Synthesis of substituted $1H$ -phospholes



Angew. Chem. Int. Ed. **2014**, *53*, 4587



Russ. Chem. Bull. **2020**, *69*, 1185

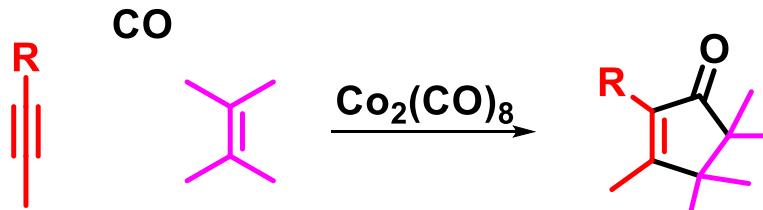


Dalton Trans. **2018**, *47*, 11521

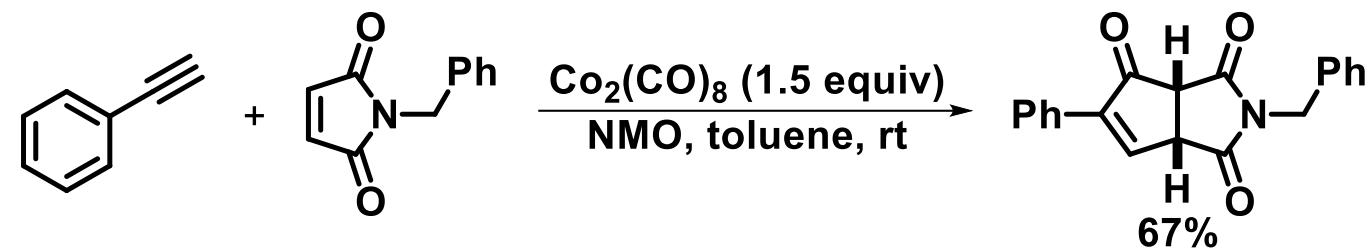
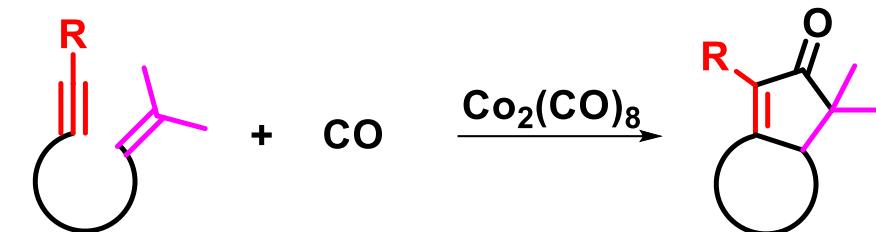
Cycloisomerization and cyclization reactions

► Metallacycles

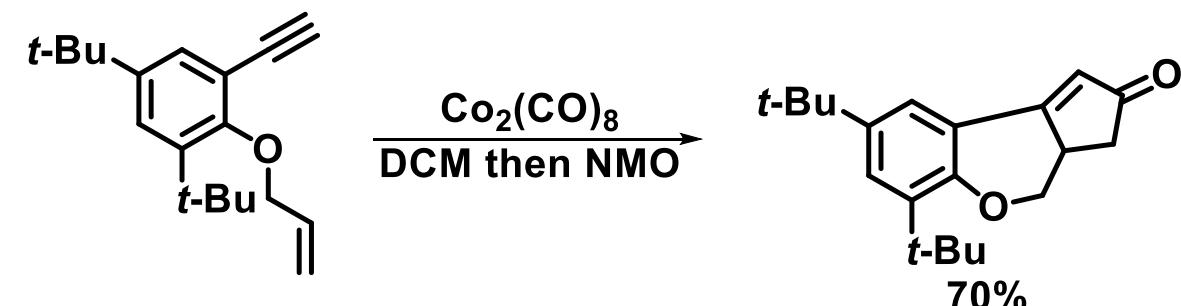
- Pauson-Khand reaction
 - Intermolecular variant



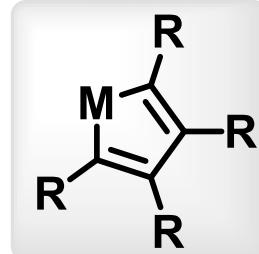
- Intramolecular variant



Tetrahedron Lett. 2017, 58, 4519



Org. Lett. 2001, 3, 2607

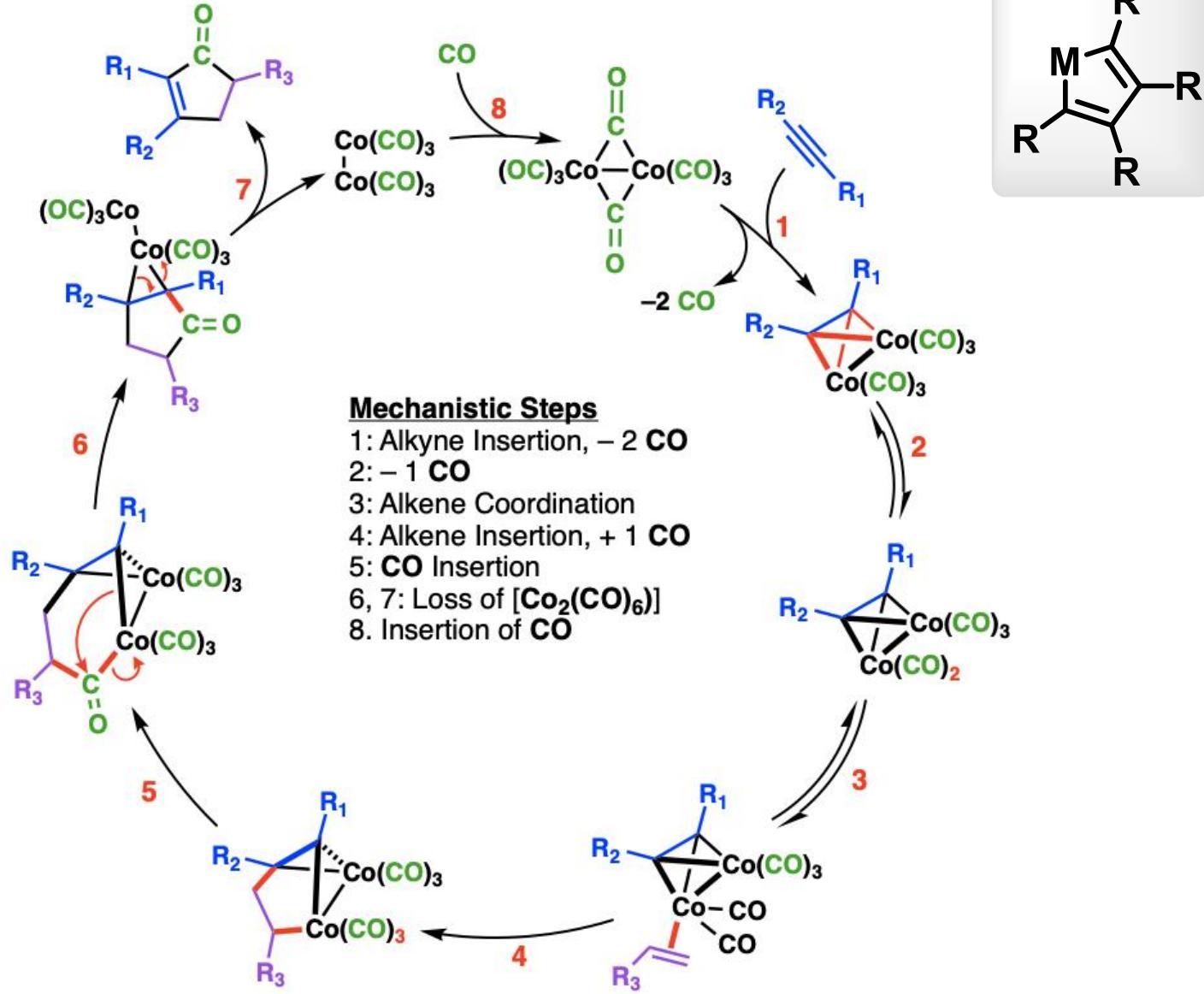


Cycloisomerization and cyclization reactions

➤ Metallacycles

- Pauson-Khand reaction

- Proposed mechanism for Pauson-Khand reaction



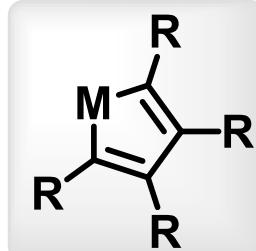
https://en.wikipedia.org/wiki/Pauson%E2%80%93Khand_reaction

Cycloisomerization and cyclization reactions

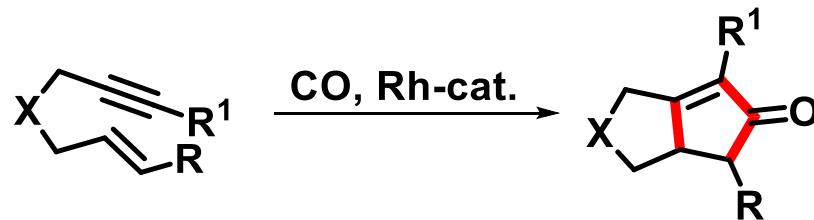
➤ Metallacycles

- Pauson-Khand type reactions
 - Ruthenium catalyzed [2+2+1] carbocyclization

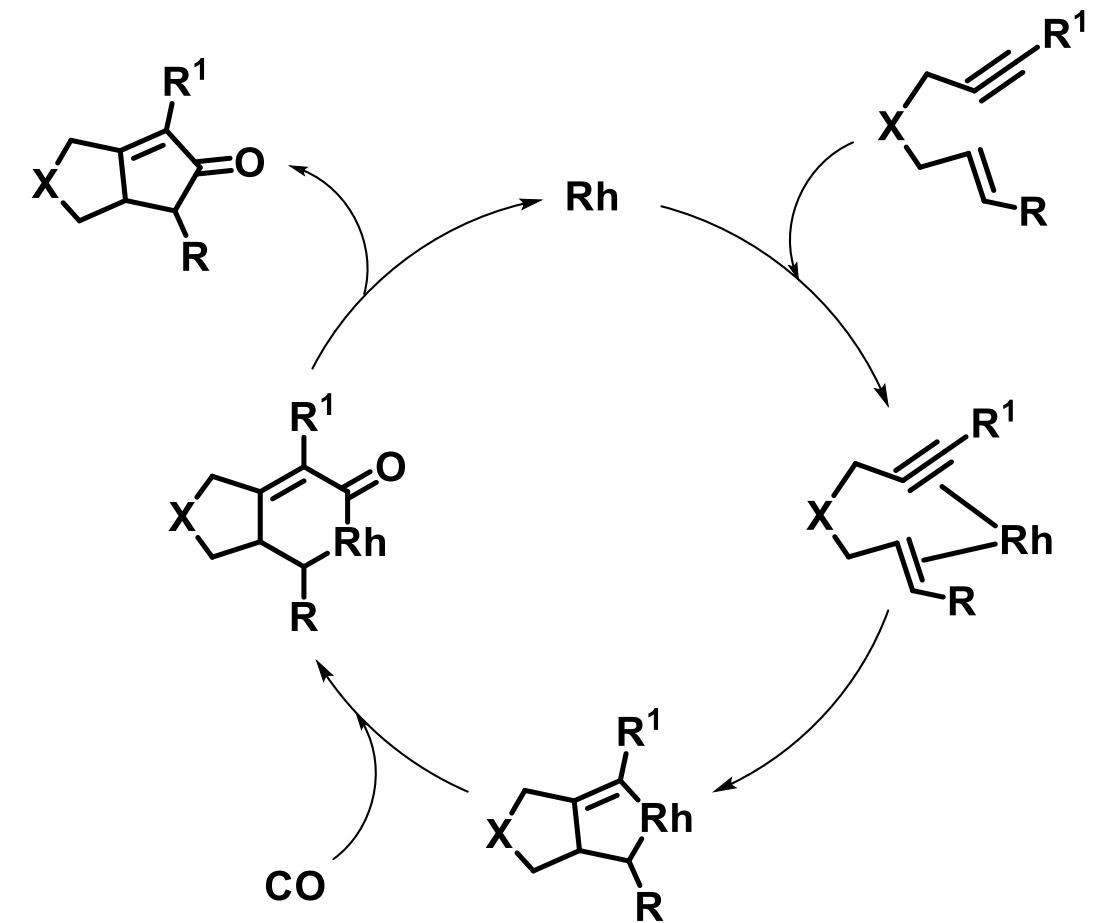
✓ Proposed mechanism



✓ General reaction scheme



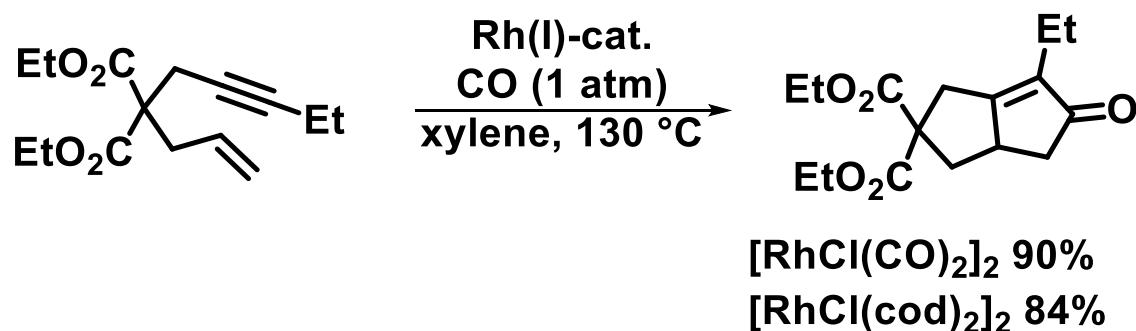
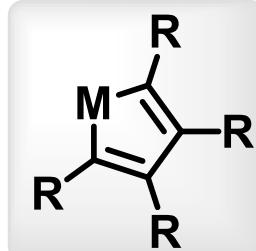
- For review see: *Acc. Chem. Res.* 2015, 48, 935



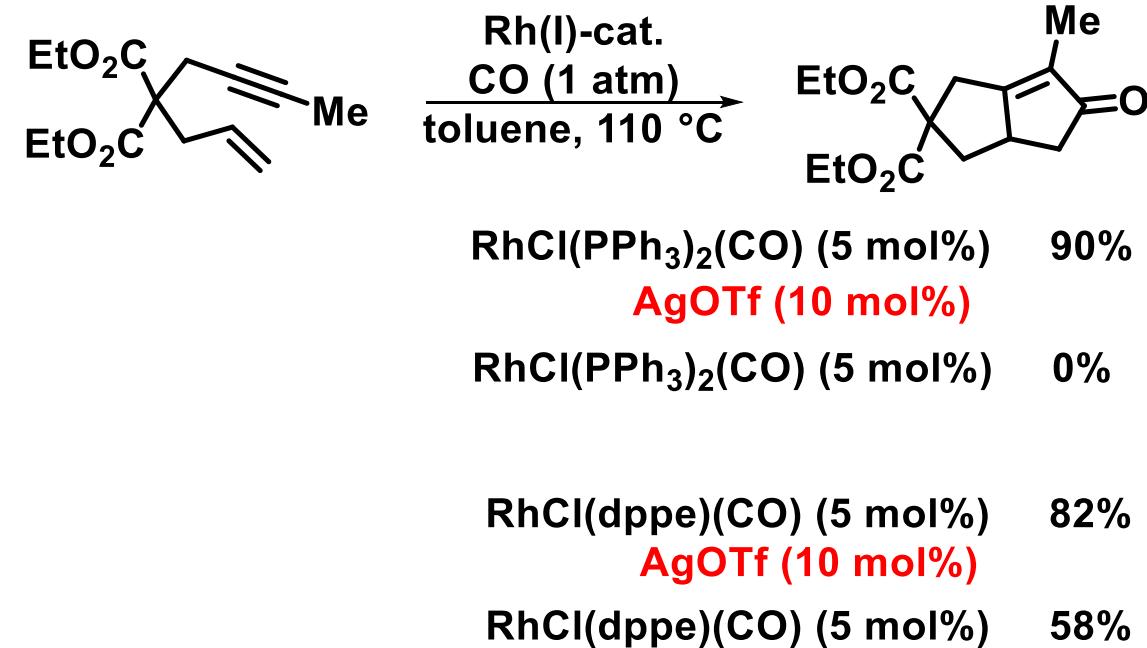
Cycloisomerization and cyclization reactions

► Metallacycles

- Pauson-Khand type reactions
 - Ruthenium catalyzed [2+2+1] carbocyclization



J. Organomet. Chem. 2001, 624, 73

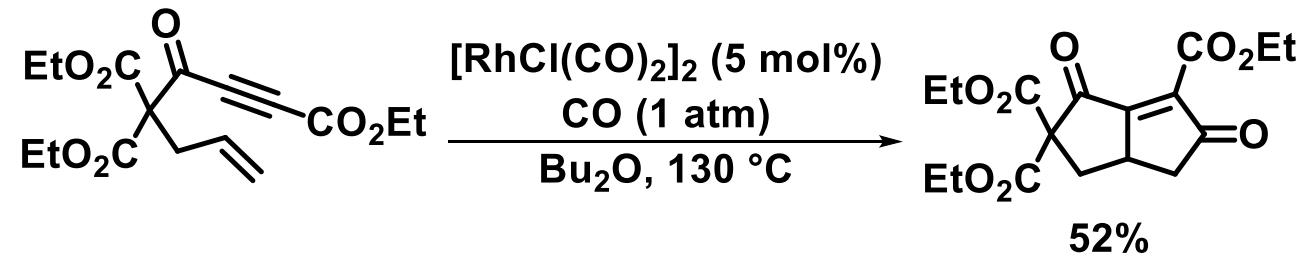
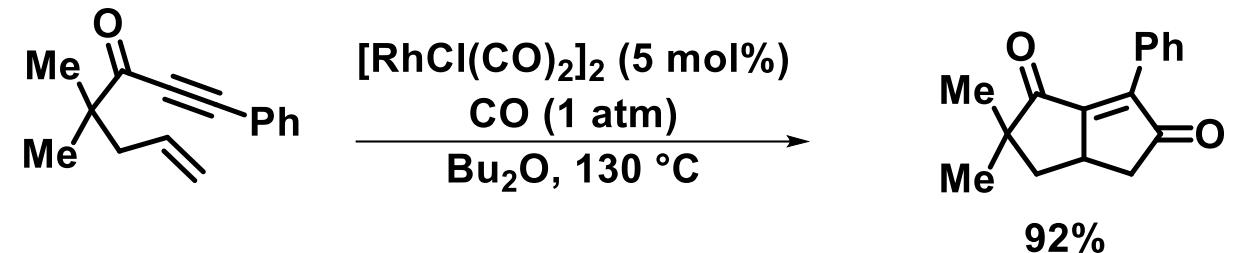
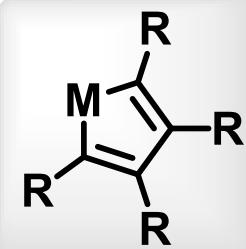


Organometallics 1998, 17, 3642

Cycloisomerization and cyclization reactions

► Metallacycles

- Pauson-Khand type reactions
 - Ruthenium catalyzed [2+2+1] carbocyclization

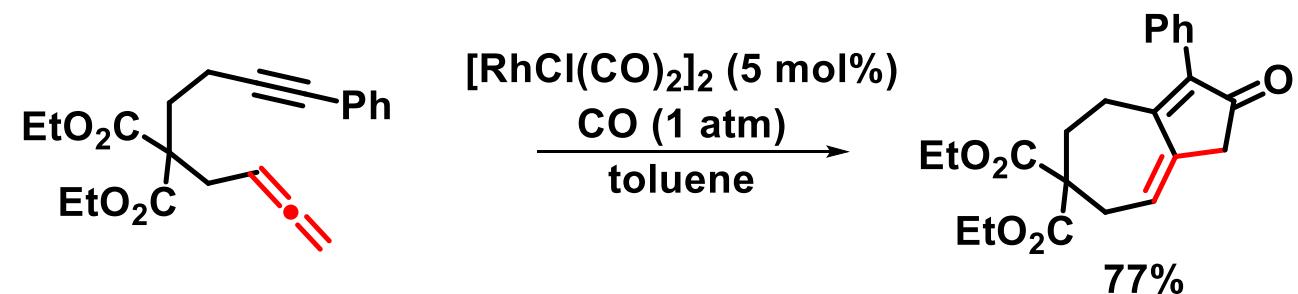
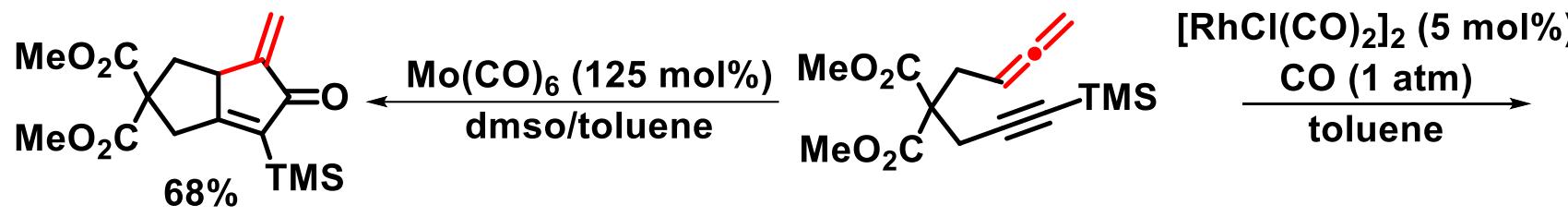
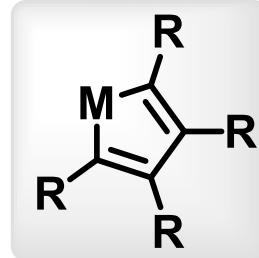


J. Organometal. Chem. **2001**, 624, 73

Cycloisomerization and cyclization reactions

► Metallacycles

- Pauson-Khand type reactions
 - Ruthenium catalyzed [2+2+1] carbocyclization



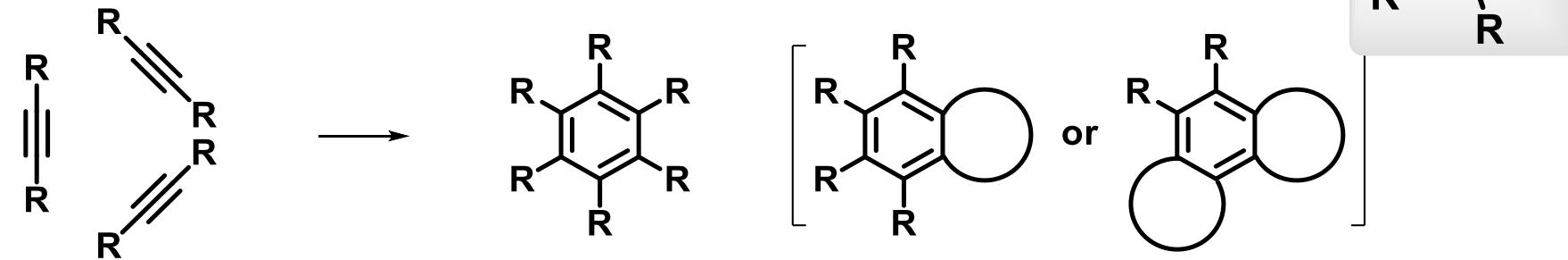
Org. Lett. **2002**, *4*, 1931; *Org. Lett.* **2002**, *4*, 1755

Cycloisomerization and cyclization reactions

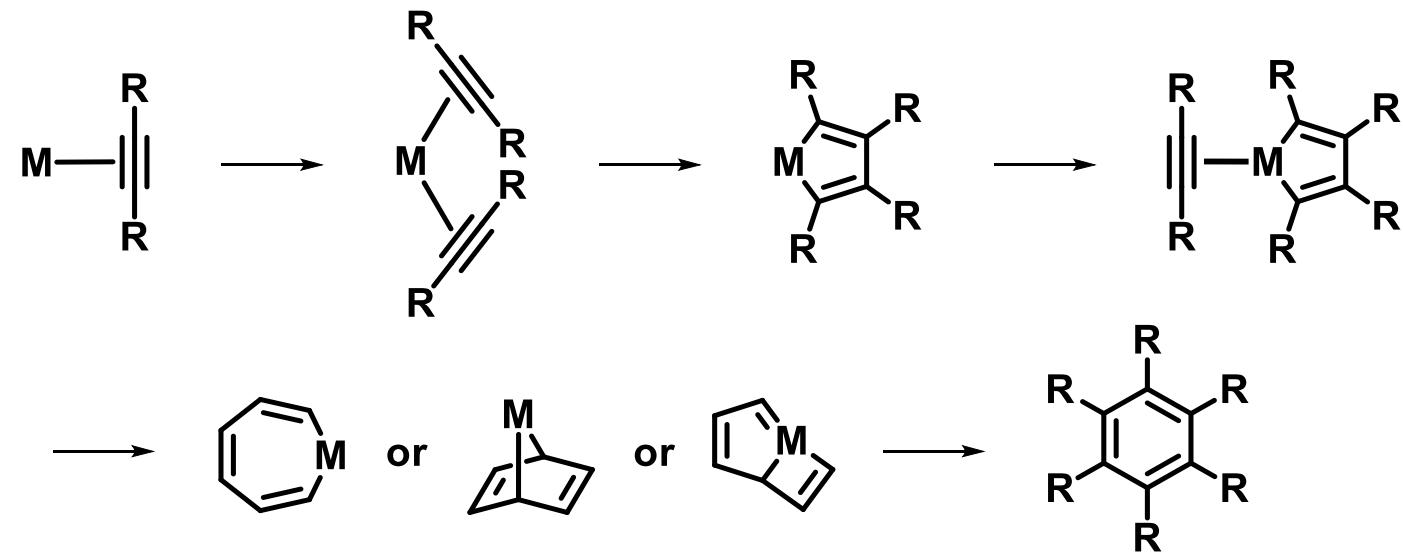
➤ Metallacycles

- [2+2+2]-cyclotrimerization reactions

- Reaction scheme



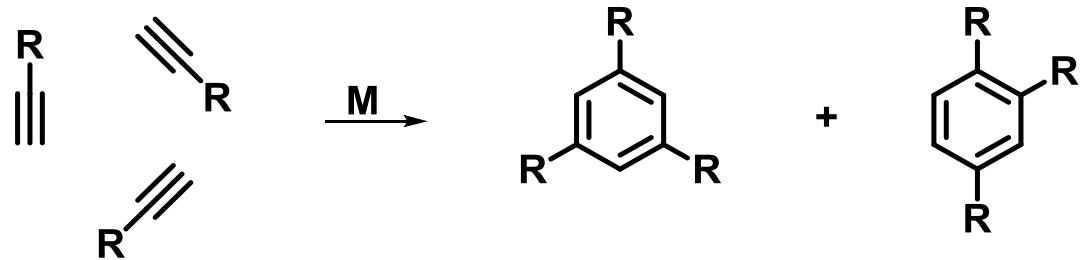
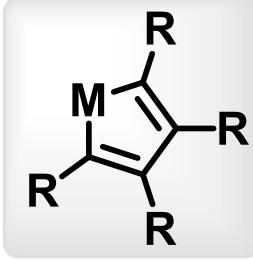
- Intermediates en route to substituted benzenes



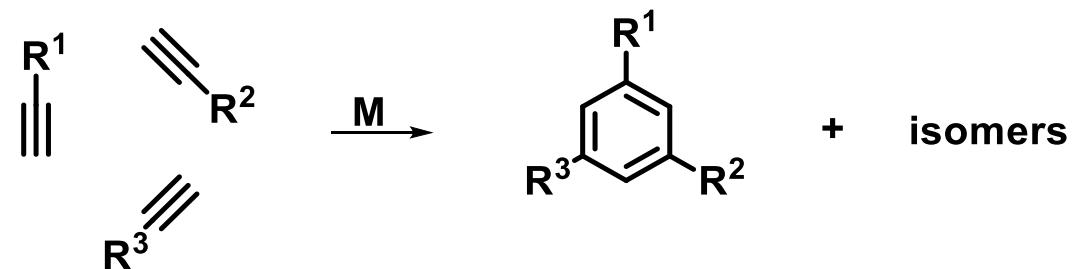
Cycloisomerization and cyclization reactions

► Metallacycles

- [2+2+2]-cyclotrimerization reactions
 - Regioselectivity in homotrimerization



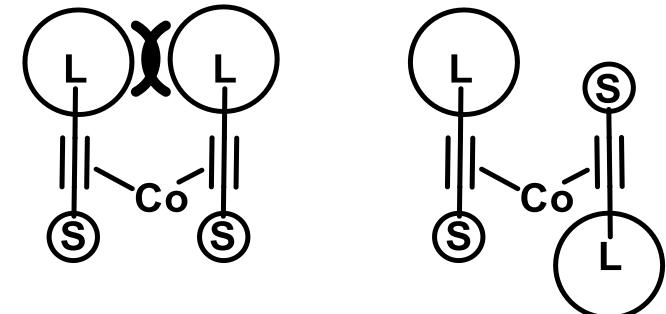
- Regioselectivity in heterotrimerization



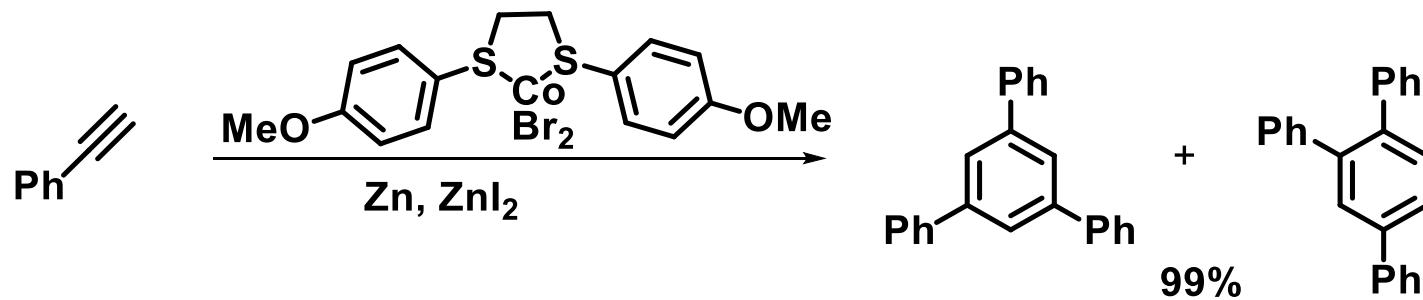
Cycloisomerization and cyclization reactions

➤ Metallacycles

- [2+2+2]-cyclotrimerization reactions
- A solution to regioselectivity issue – Wakatsuki-Yamazaki model



- A solution to regioselectivity issue – Solvent controlled regioselectivity



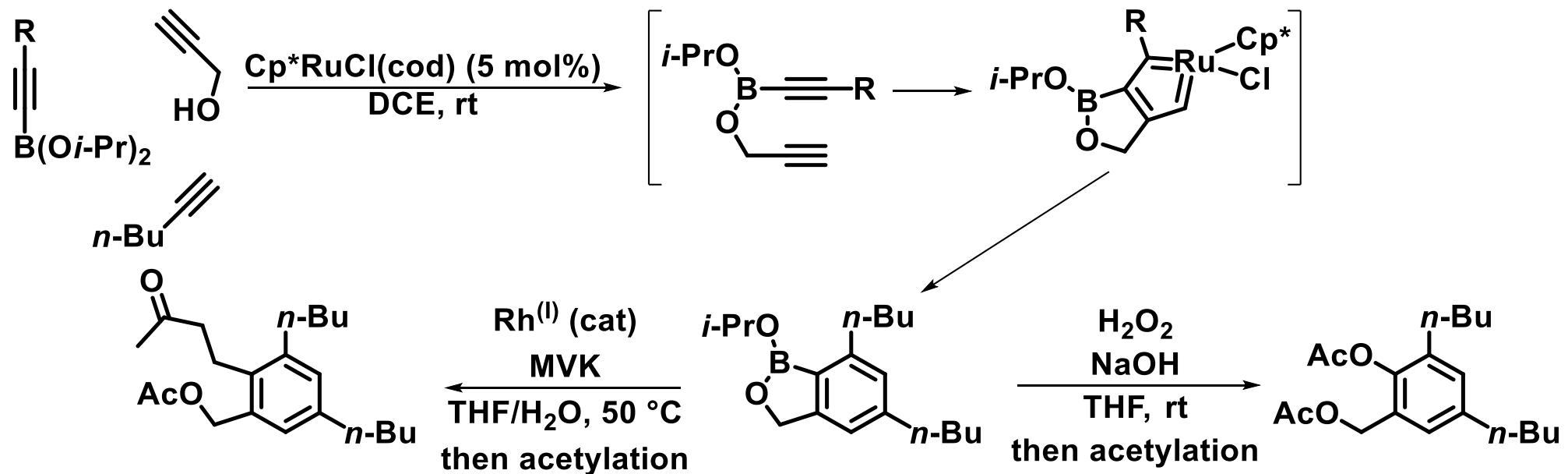
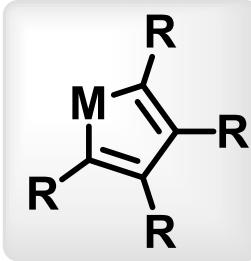
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MeCN 4:96

Eur. J. Org. Chem. 2008, 2293

Cycloisomerization and cyclization reactions

► Metallacycles

- [2+2+2]-cyclotrimerization reactions
 - A solution to regioselectivity issue – Intramolecular reaction

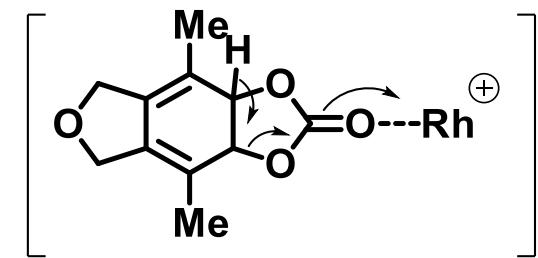
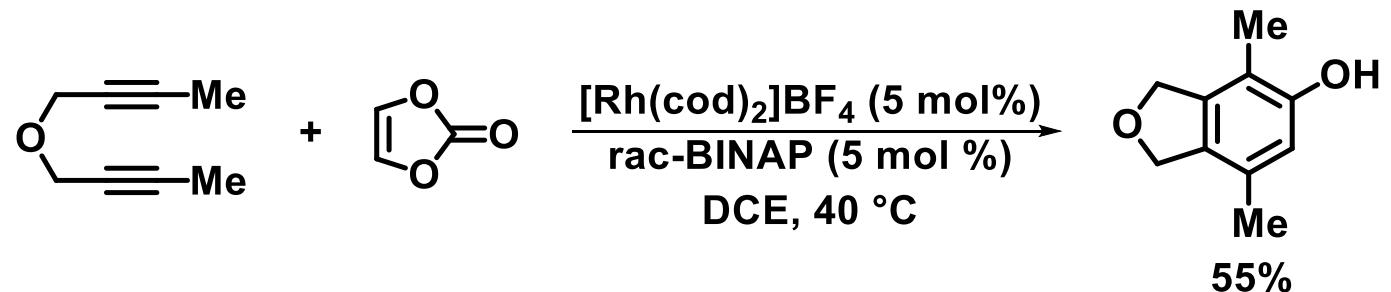
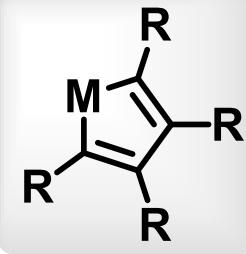


J. Am. Chem. Soc. **2004**, *126*, 3712; *J. Am. Chem. Soc.* **2005**, *127*, 9625

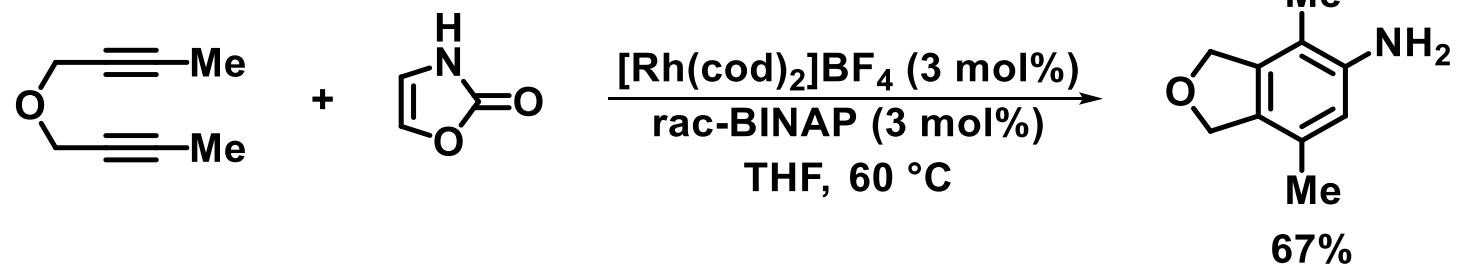
Cycloisomerization and cyclization reactions

► Metallacycles

- [2+2+2]-cyclotrimerization reactions
 - Unusual substrates



Org. Lett. **2009**, *11*, 1337

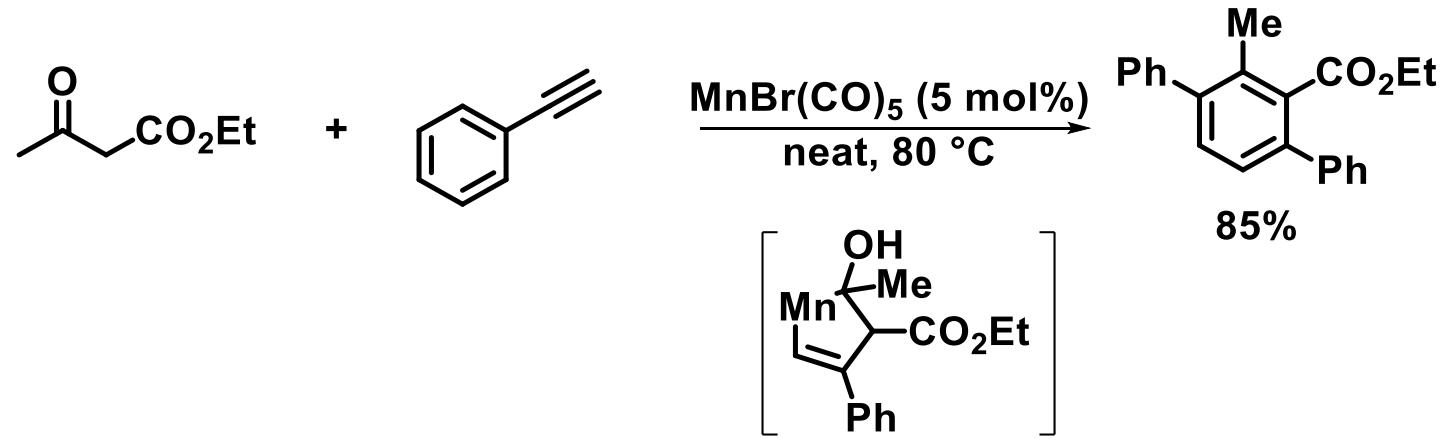
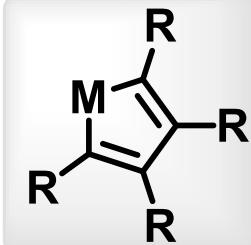


J. Org. Chem. **2011**, *76*, 4686

Cycloisomerization and cyclization reactions

► Metallacycles

- [2+2+2]-cyclotrimerization reactions
 - Unusual substrates



Org. Lett. **2008**, *10*, 3009