

# Literature Report 2011-06-07

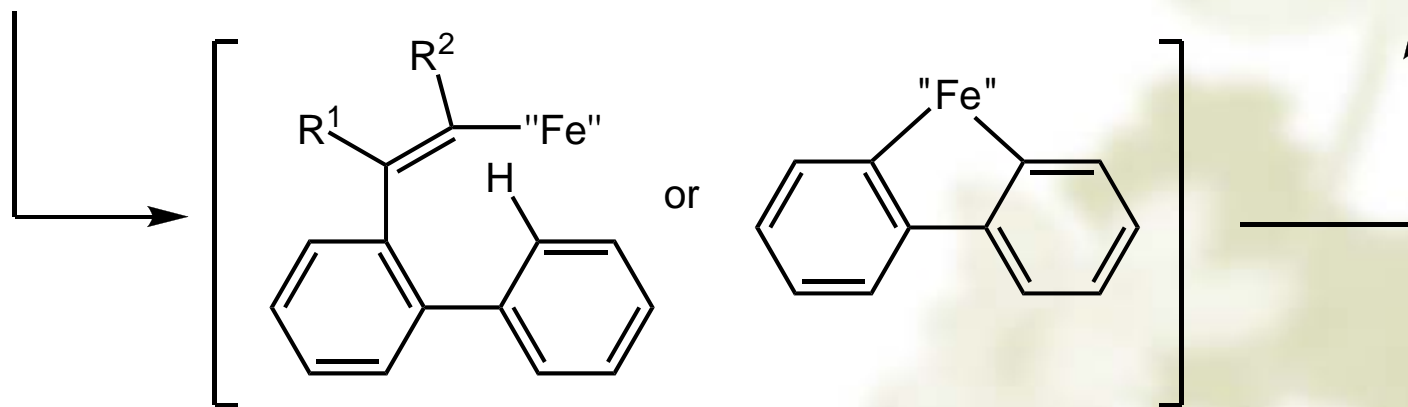
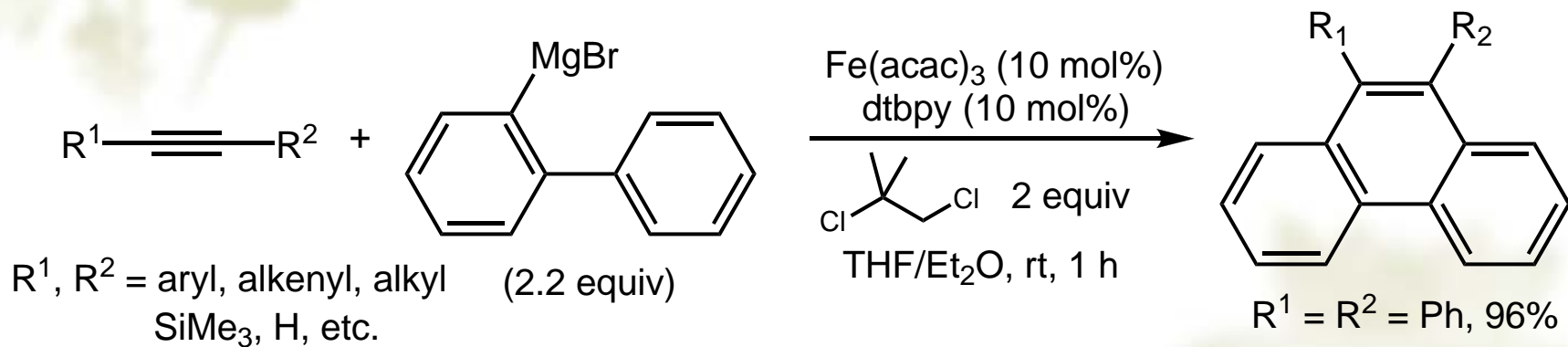
Duan, Y. Checker: Chen, Q.-A.

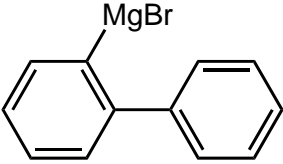
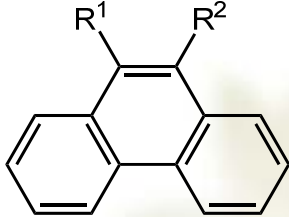
## 炔与联芳基化合物的[4+2]芳环化反应 合成菲类化合物

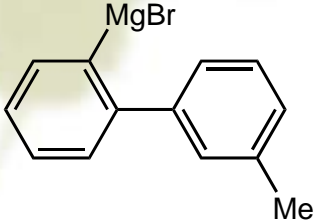
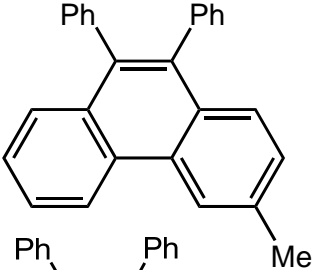
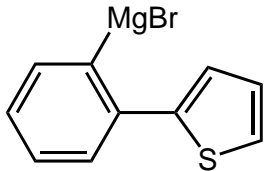
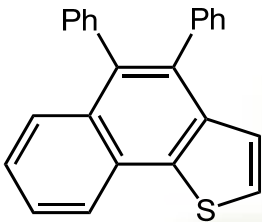
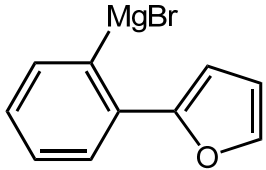
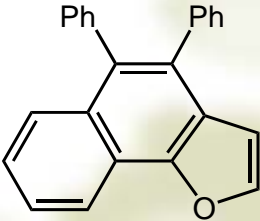
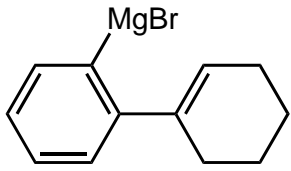
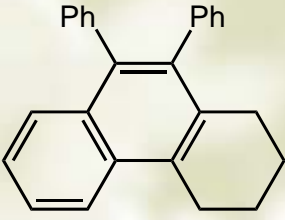
Nakamura, E.\* et al

*J. Am. Chem. Soc.* **2011**, 133, 6557

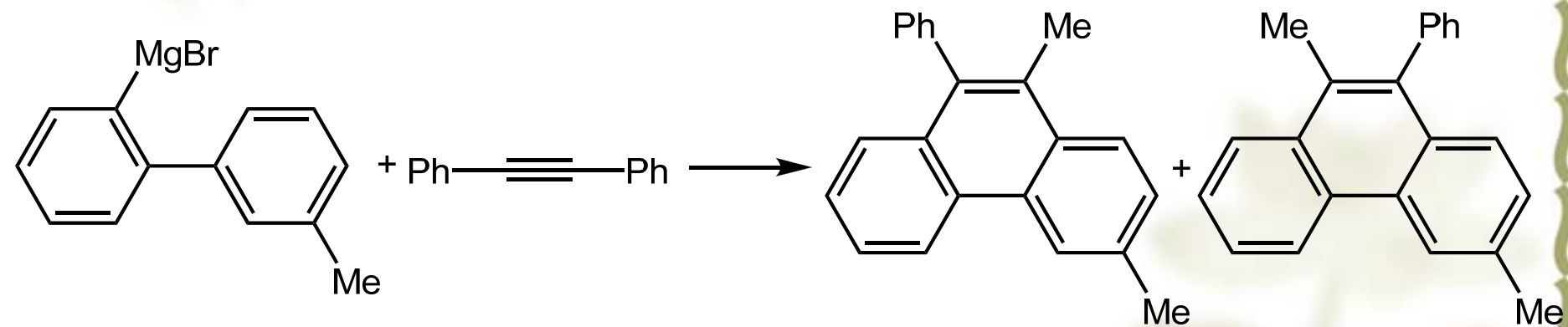
# Fe催化的 [4+2] 苯环化反应



Entry	ArMgBr	R <sup>1</sup>	R <sup>2</sup>	Product	Yield (%)
1		Ph	Ph		96
2		Ph	4-ClC <sub>6</sub> H <sub>4</sub>		77
3		Ph	4-BrC <sub>6</sub> H <sub>4</sub>		75
4		Ph	4-MeOC <sub>6</sub> H <sub>4</sub>		95
5		Ph	4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>		95
6		Ph	( <i>E</i> )-CH=CHC <sub>6</sub> H <sub>4</sub>		79
7		Ph	CF <sub>3</sub>		69
8		Ph	Me		95
9		<i>n</i> -Pr	<i>n</i> -Pr		91
10		SiMe <sub>3</sub>	SiMe <sub>3</sub>		59
11		Ph	H		44

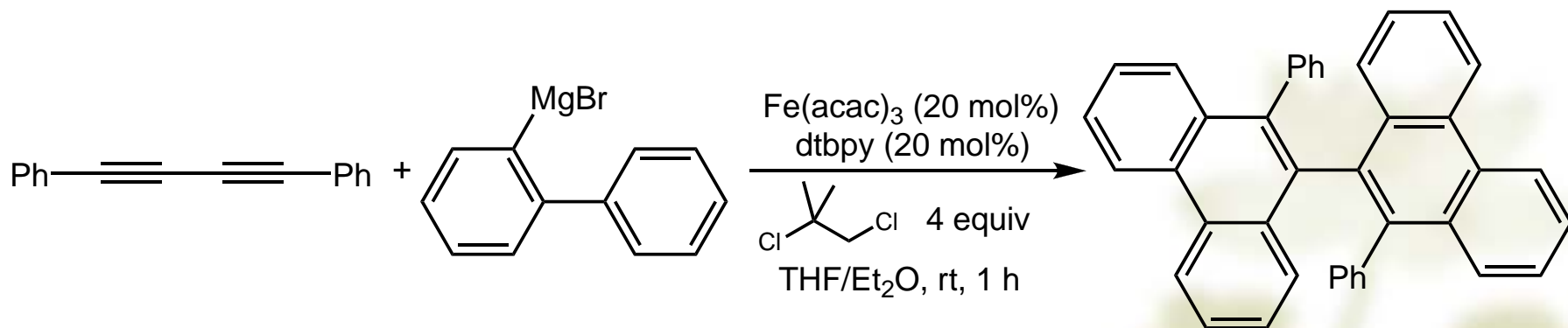
Entry	ArMgBr	R <sup>1</sup>	R <sup>2</sup>	Product	Yield (%)
12		Ph	Ph		89
13		Ph	Ph		41
14		Ph	Ph		39
15		Ph	Ph		85

## 非对称底物



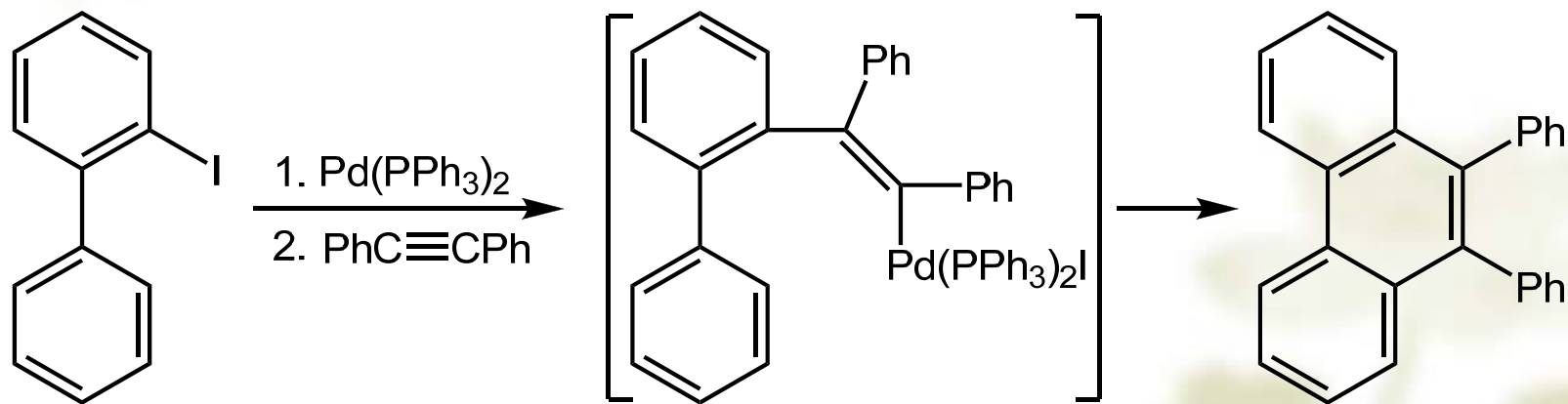
Yield: 93%, 55 : 45

## 二炔的苯环化反应



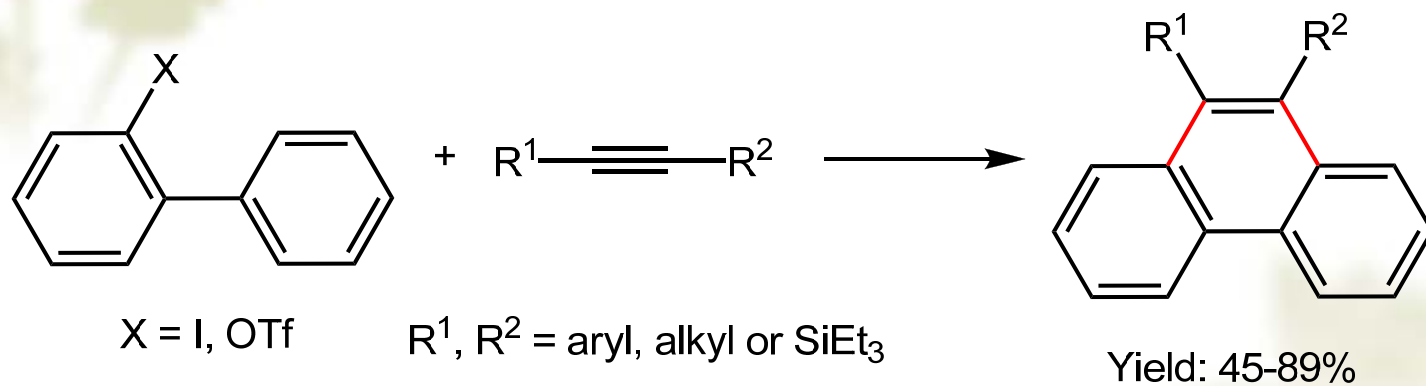
Yield: 55%

## Pd催化的环化反应



Heck, R. F. et al *Organometallics* 1987, 6, 1941

## Pd催化的苯环化反应



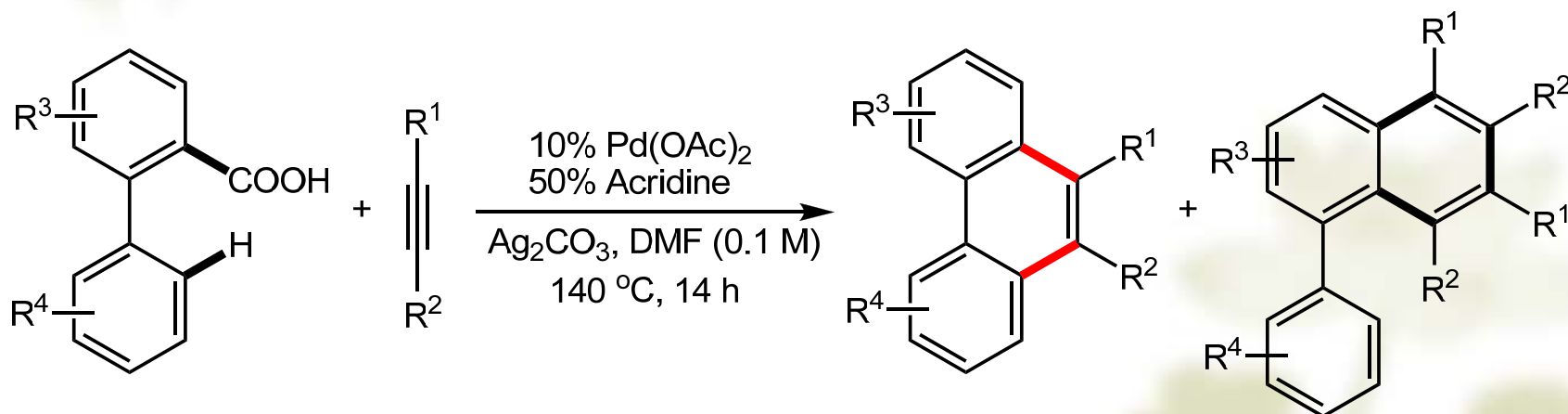
Procedure A: Pd(OAc)<sub>2</sub> (5 mol%), NaOAc (2 eq.), LiCl (1 eq.), DMF, 100 °C

Procedure B: Pd(OAc)<sub>2</sub> (5 mol%), NaOAc (2 eq.), *n*-Bu<sub>4</sub>NCl (3 eq.), DMF, 100 °C

Larock, R. C. et al *J. Org. Chem.* **1997**, *62*, 7536

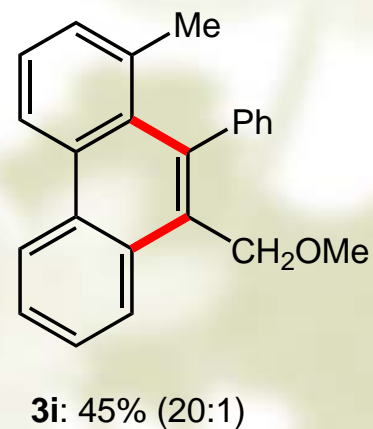
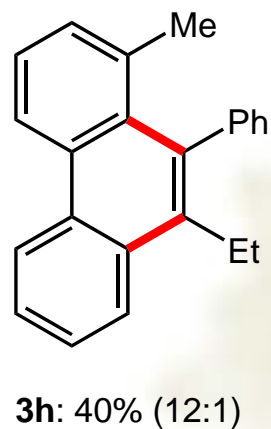
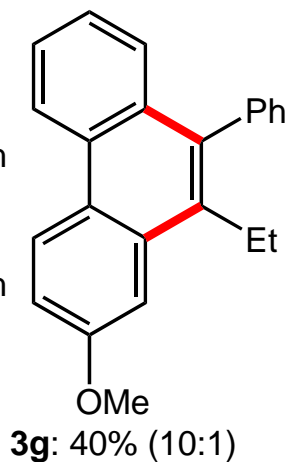
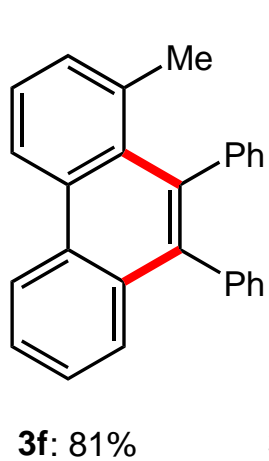
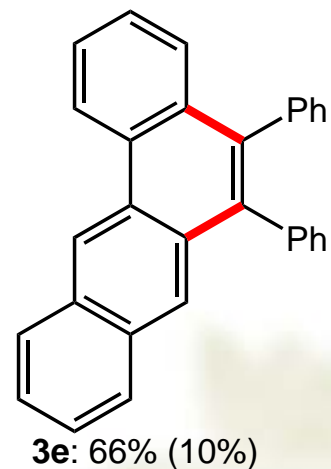
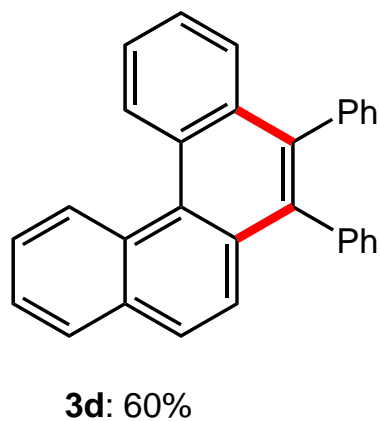
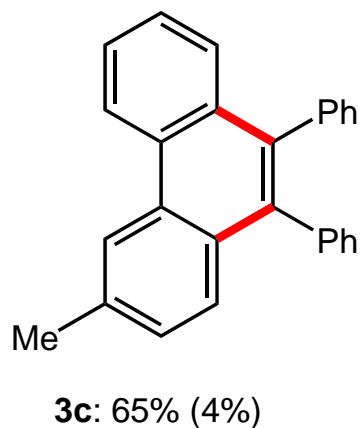
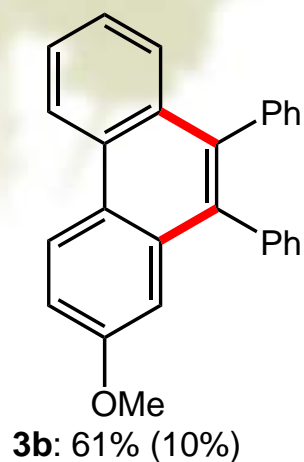


## Pd催化的脱羧偶联苯环化反应

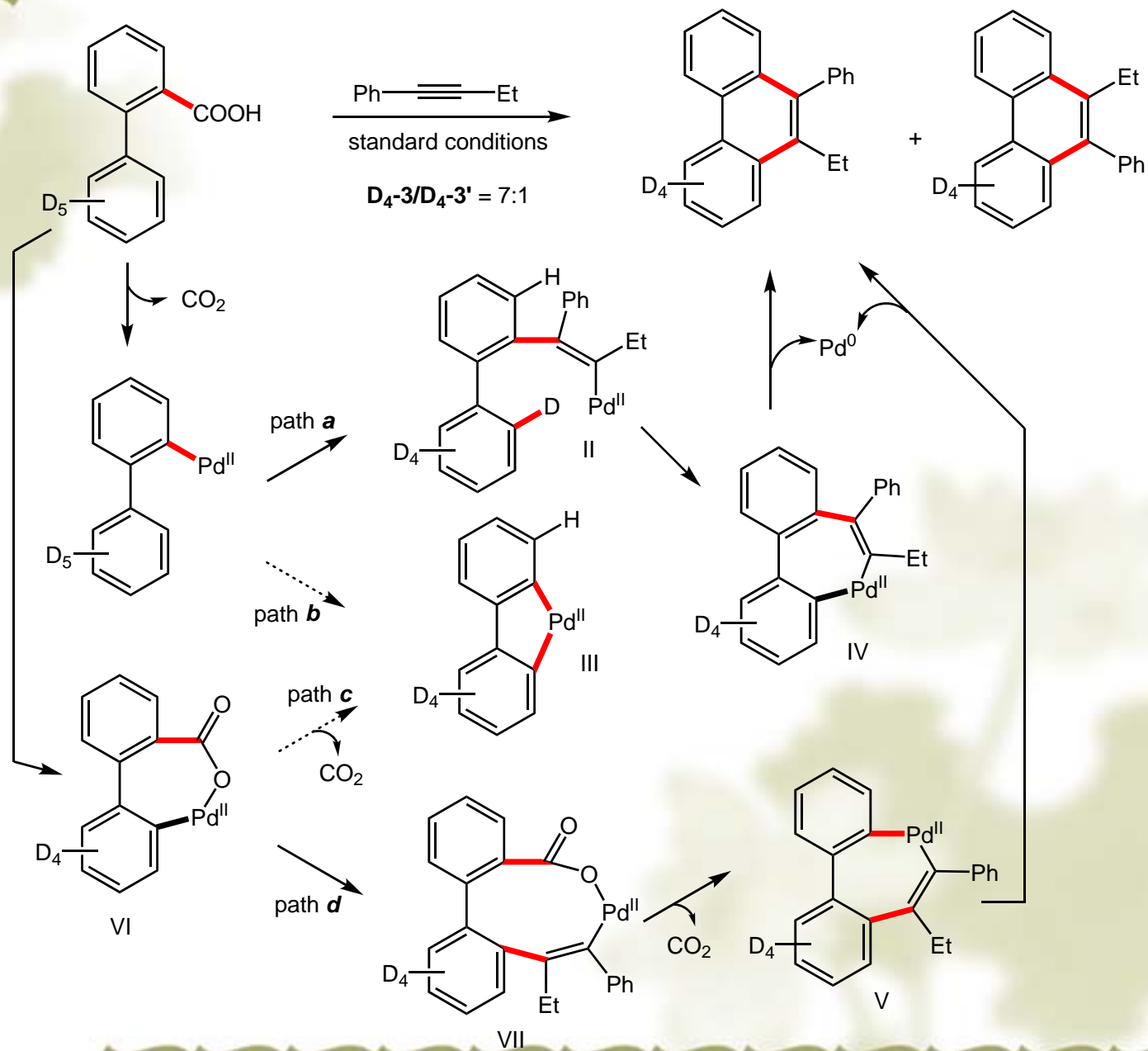


Wang, C. et al *J. Am. Chem. Soc.* **2010**, 132, 14006

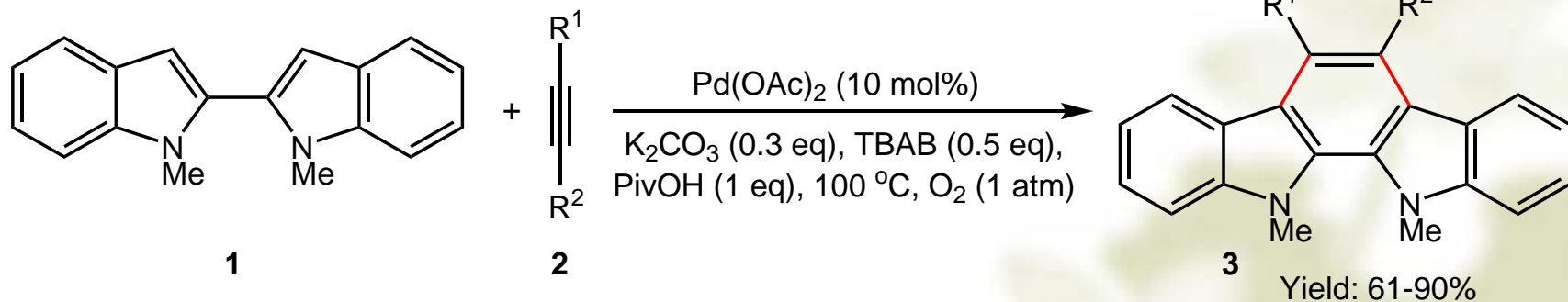
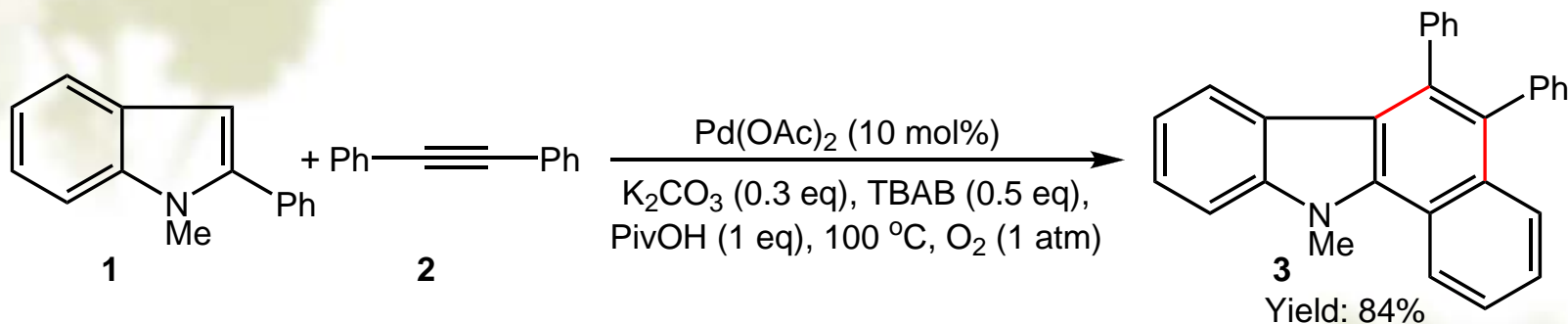
## Pd催化的脱羧偶联苯环化反应



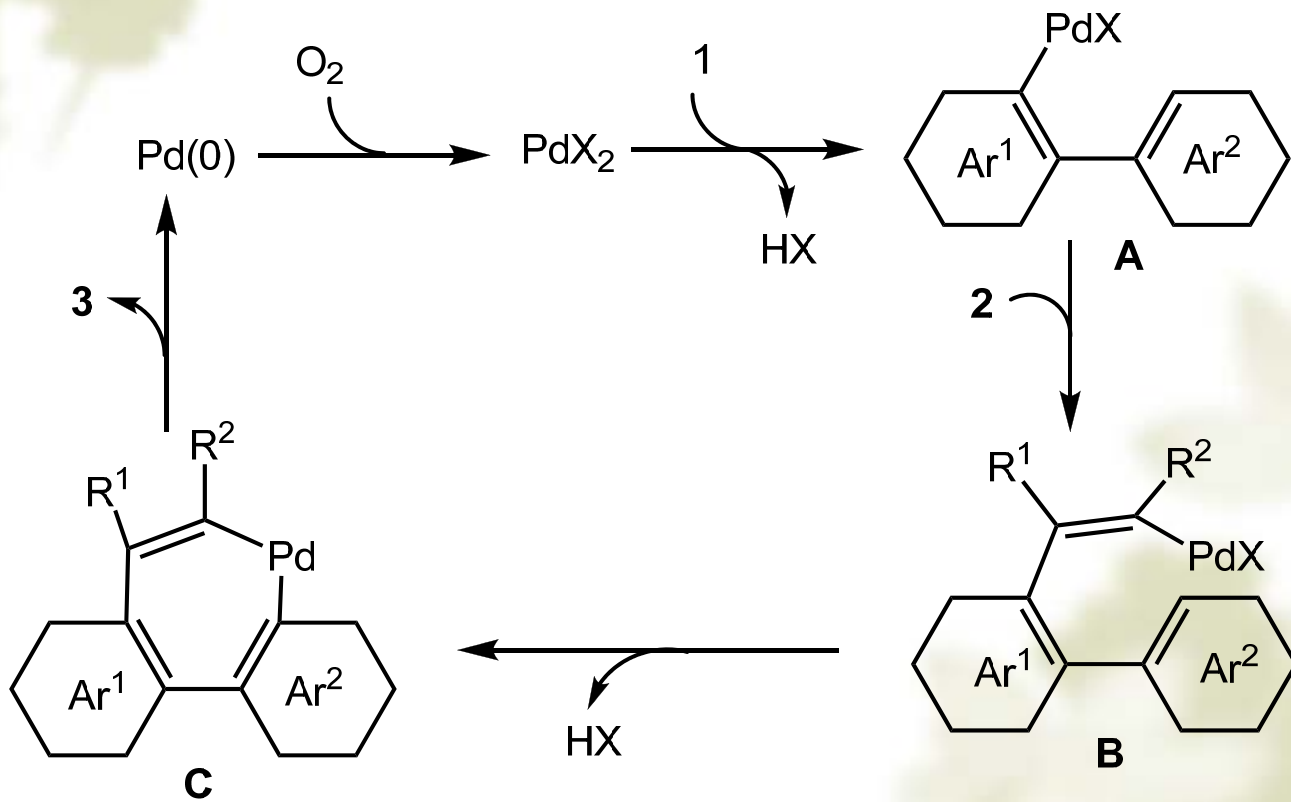
# 机理



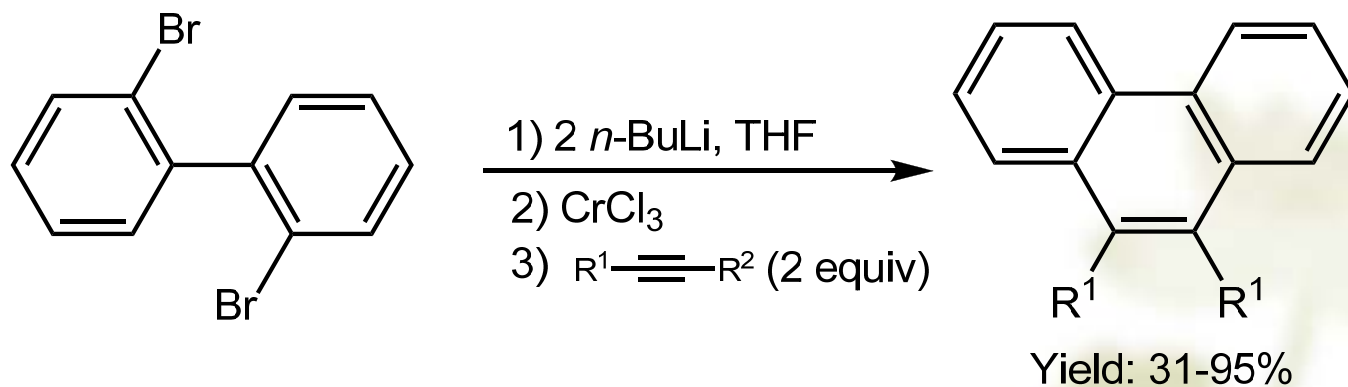
## Pd催化的C-H 和C-C 键活化/芳环化反应



# 机理

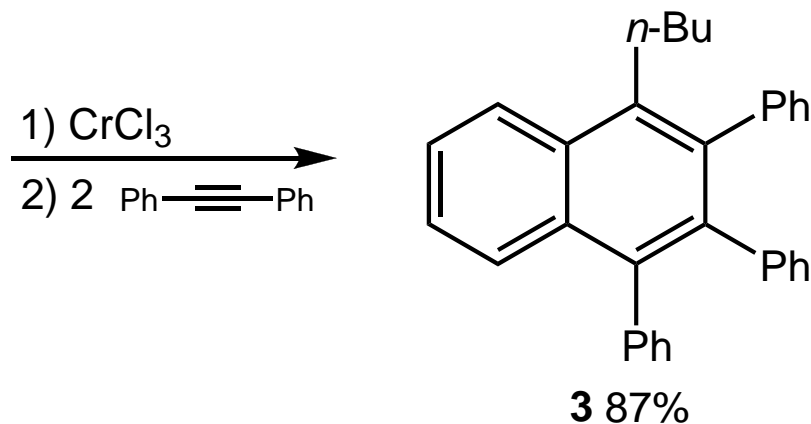
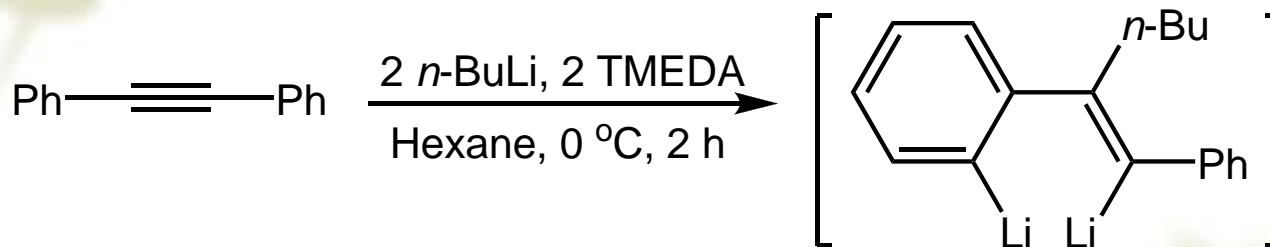


## Cr促进的苯环化反应



R<sup>1</sup>, R<sup>2</sup> = H, alkyl, alkynyl, TMS, CO<sub>2</sub>R etc.

## Cr促进的苯环化反应



Takahashi, T. et al *Org. Lett.* **2005**, 7, 5453

❖ Phenanthrene is an important organic structure in materials science, and it is also a partial structure of superconducting picene and carbon nanotubes. Among the numerous synthetic routes to the phenanthrene class of aromatics, the [4+2] benzannulation reaction between an alkyne and a biaryl compound has not attracted much attention, despite its ability to create quickly a large variety of phenanthrene compounds. We report herein an iron-catalyzed coupling between an internal or terminal alkyne and a biaryl or alkenylaryl Grignard reagent that forms 9-substituted and 9,10-disubstituted phenanthrenes and congeners in moderate to excellent yields.



❖ In summary, we have developed a new [4+2] benzannulation method that allows the coupling of a variety of alkynes with diaryl and related Grignard reagents. Because of the high activity of the iron-based catalytic system, this reaction takes place under mild conditions and enables the construction of sterically congested systems. The oxidative coupling conditions allow the reaction to take place with remarkable chemoselectivity, such as the tolerance of bromide, chloride, trimethylsilyl, trifluoromethyl, and olefinic groups. Some evidence suggests the involvement of a ferracycle intermediate, an intriguing mechanistic possibility under investigation in our laboratory.