Literature Report

Nickel-Catalyzed Stereoselective Diarylation of Alkenylarenes

Reporter: Chang-Bin Yu

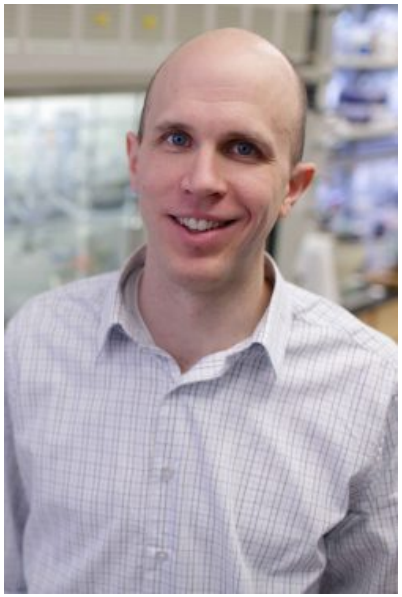
Checker: Yang Zhao

October 29, 2018

Dalian Institute of Chemical Physics

Gao, P.; **Brown, M, K.** *et al. J. Am. Chem. Soc.* **2018**, *140,* 10653.

CV of Prof. Brown, M. K.



Prof. Brown, M. K.

1998-2002	B.S. (Hamilton College)
2002-2008	Ph.D. (Boston College)
2008-2011	Postdoc. (Harvard University)
2011-2016	Assistant Prof. (Indiana University)
2016-now	Associate Prof. (Indiana University)

Research Fields:

- Stereoselective [2+2] Cycloadditions
- Transition Metal-Catalyzed Cross-Coupling

Contents

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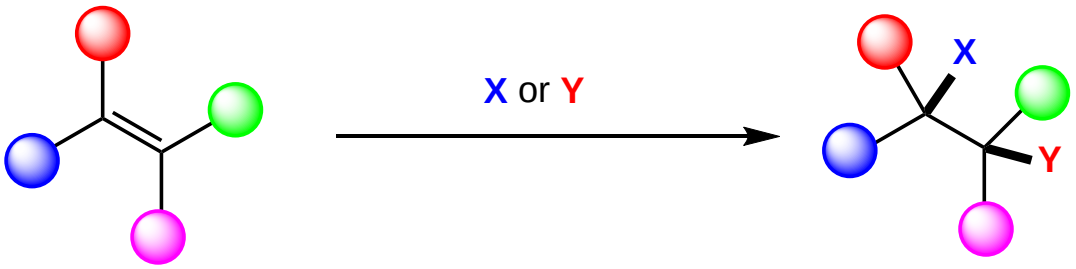
Difunctionalization of Olefins

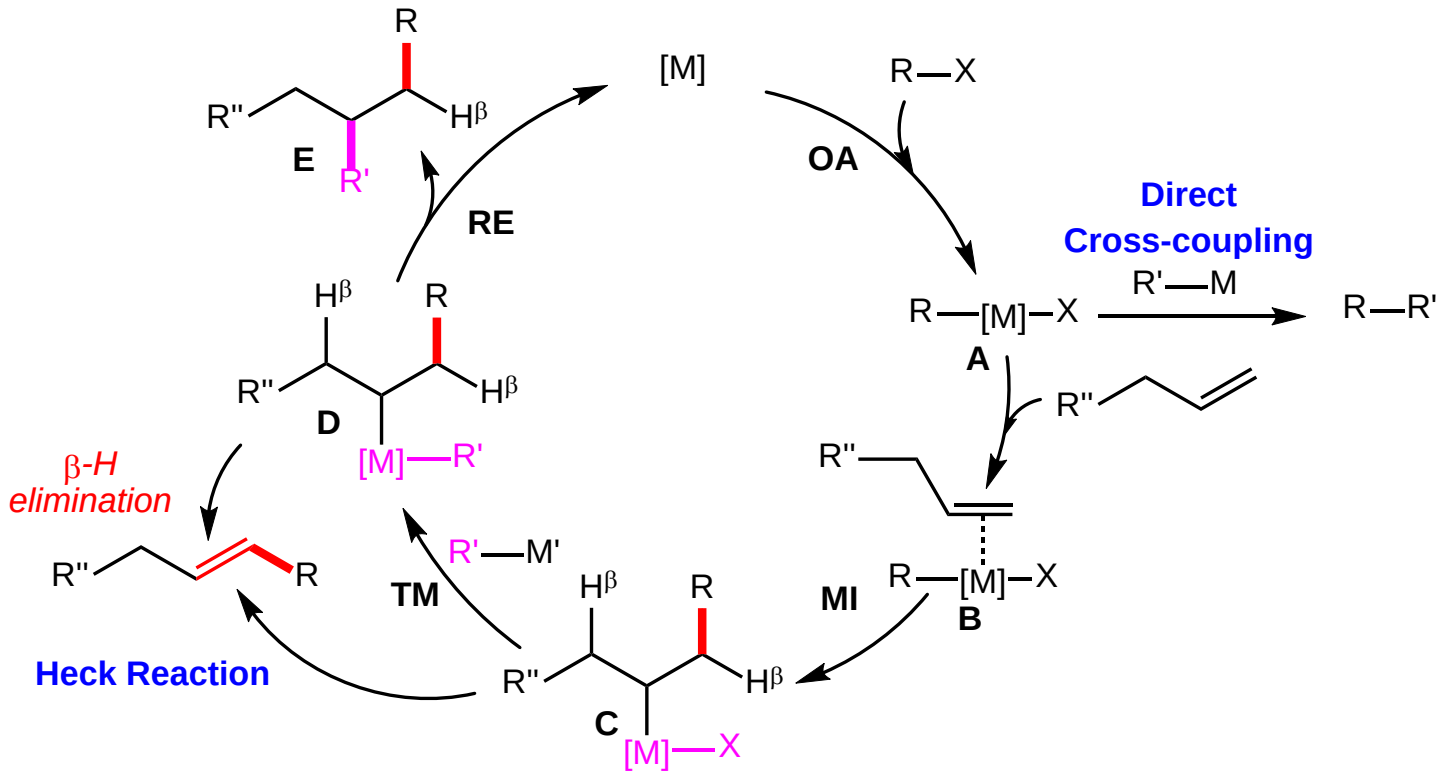


X or Y = H, halogen, sulfor, oxygen, carbon, nitrogen *et al.*

烯烃双官能化是合成诸多天然产物的重要途径之一，也为构建多样性的化学结构提供了有力的手段。近年来研究主要集中在过渡金属催化的烯烃碳氧化、氧氮化、氧硫化、硫卤化和硫氮化等几类反应。

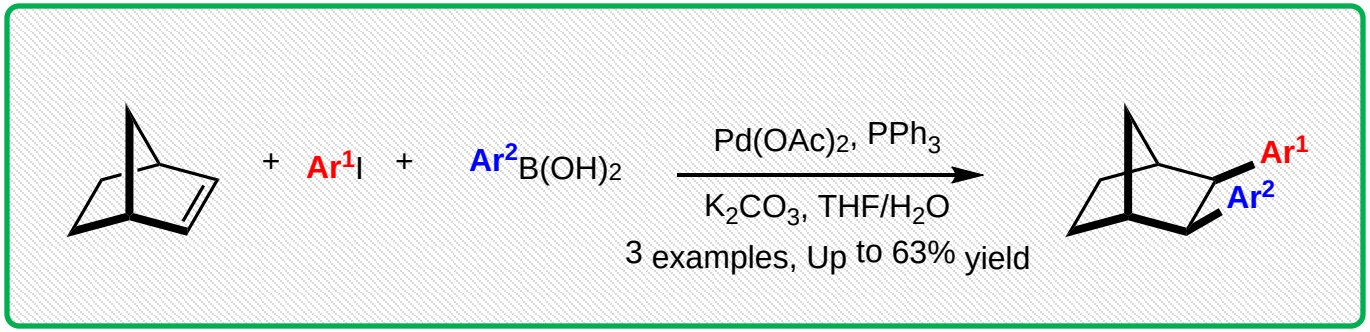
Dicarbofunctionalization of Olefins

Catalytic Cycle and Side Reaction

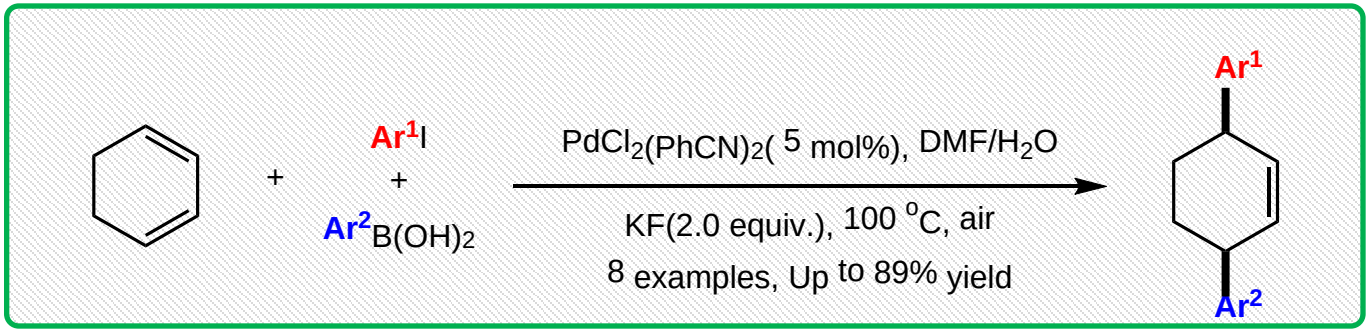


Shekhar, K. H.; **Giri, R.** *et al. J. Org. Chem*. **2018**, *83*, 3013.

Diarylation of 1,2-Disubstituted Alkenes

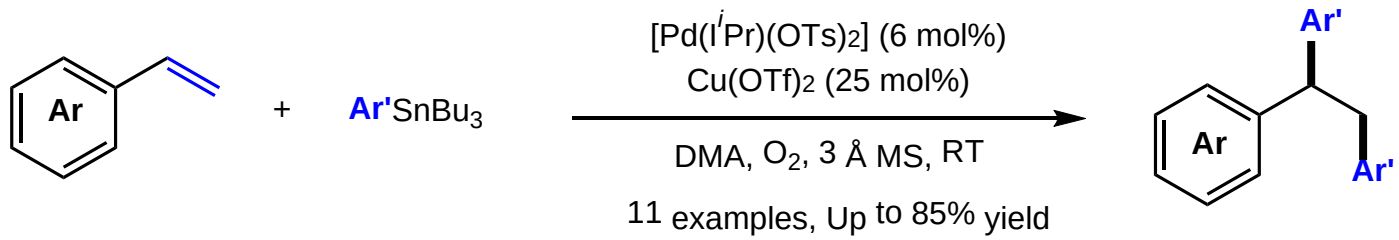


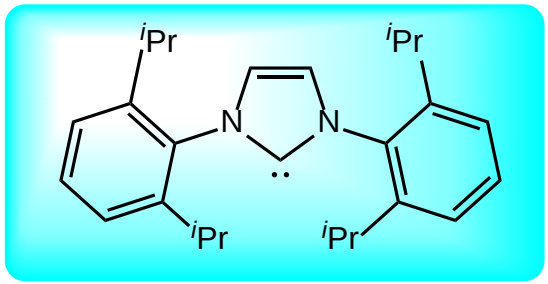
Ahaulis, K. M.; **Goodson, F. E.** *et al. J. Org. Chem.* **2002**, *67*, 5860.



Zhang, X.-X.; **Larock, R. C.** *et al. Tetrahedron* **2010**, *66*, 4265.

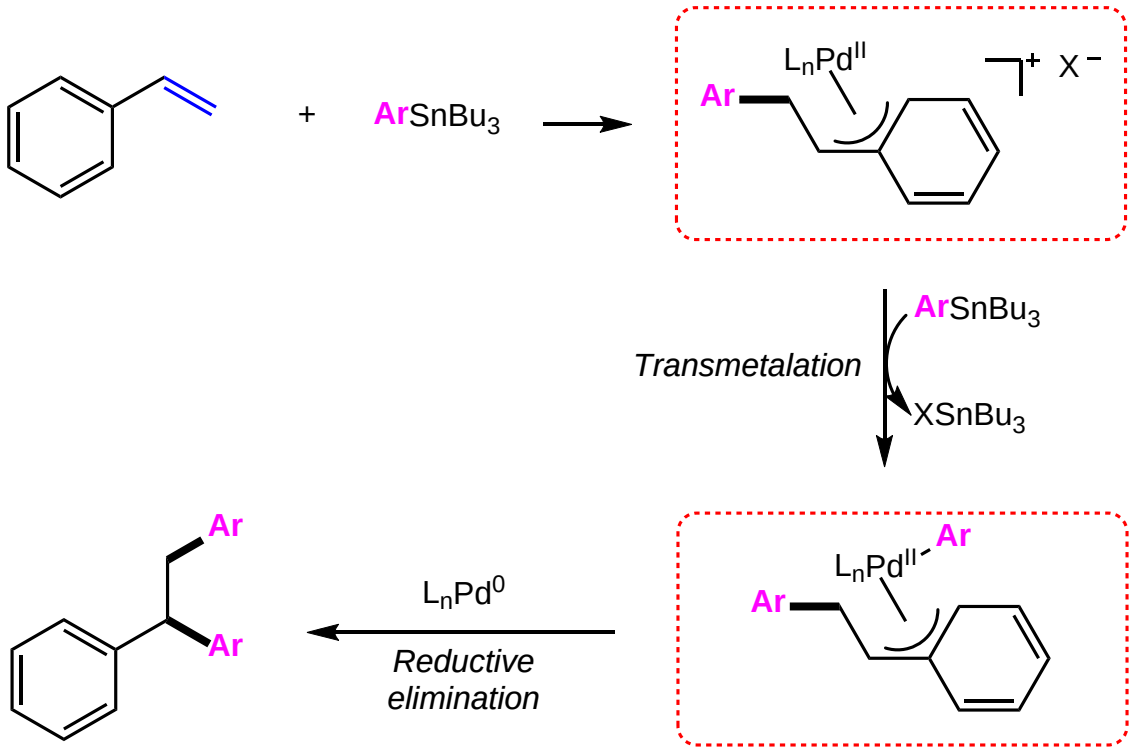
Pd-catalyzed Diarylation of Terminal Alkenes





Urkalan, K. B.; **Sigman, M. S.** *et al. Angew. Chem. Int. Ed.* **2009**, *48,* 3146.

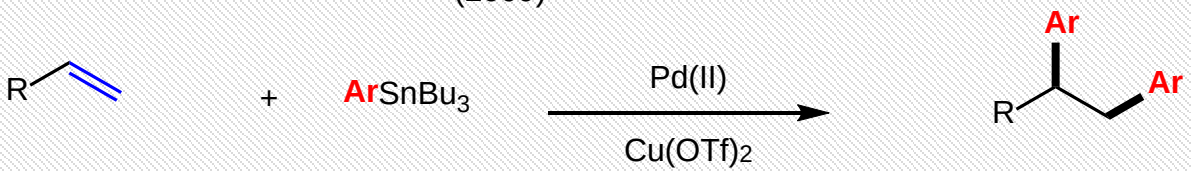
Pd-catalyzed Diarylation of Terminal Alkenes



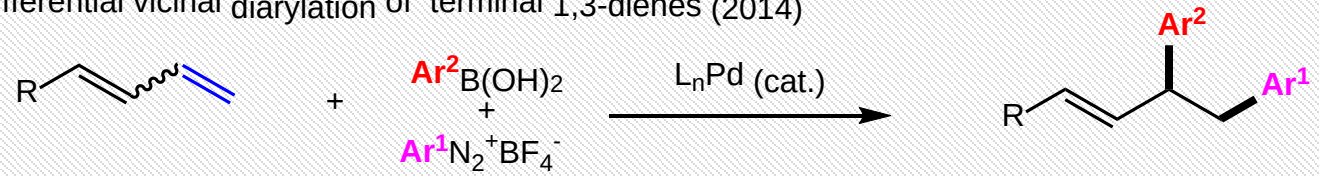
Urkalan, K. B.; **Sigman, M. S.** *et al. Angew. Chem. Int. Ed.* **2009**, *48,* 3146.

Pd-catalyzed 1,2-Diarylation of Vinylarenes

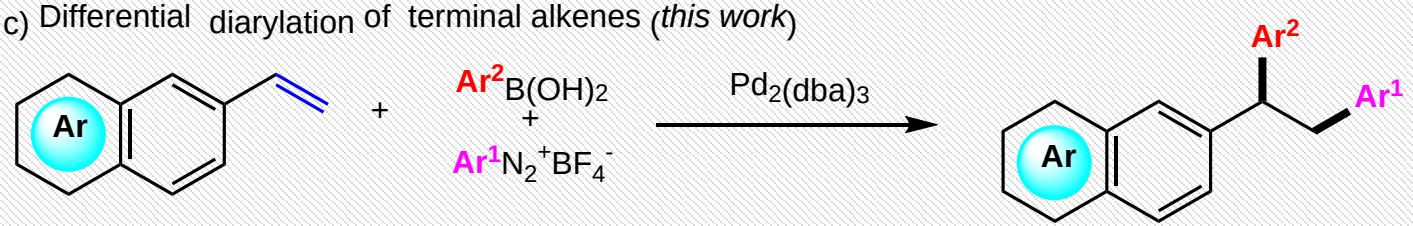
a) Difunctionalization of terminal alkenes (2009)



b) Differential vicinal diarylation of terminal 1,3-dienes (2014)

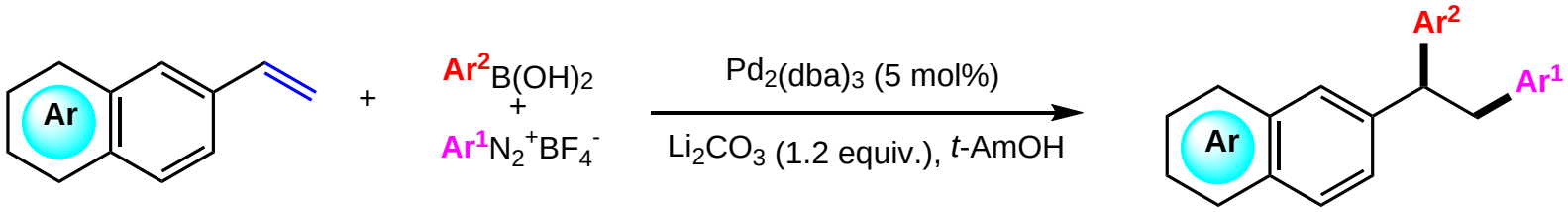


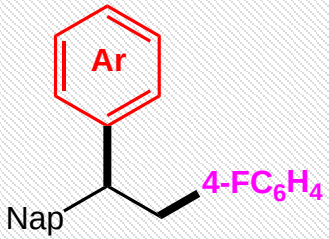
c) Differential diarylation of terminal alkenes (*this work*)



Kuang, Z.; **Song, Q.** *et al. Org. Chem. Front.* **2017**, *4*, 1224.

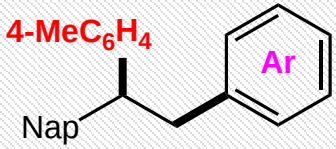
Pd-catalyzed 1,2-Diarylation of Vinylarenes





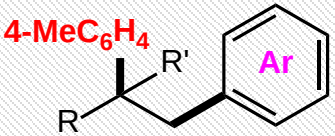
The scope of boronic acids

15 examples, 46-77% yields



The scope of aryl diazonium salts

12 examples, 42-79% yields

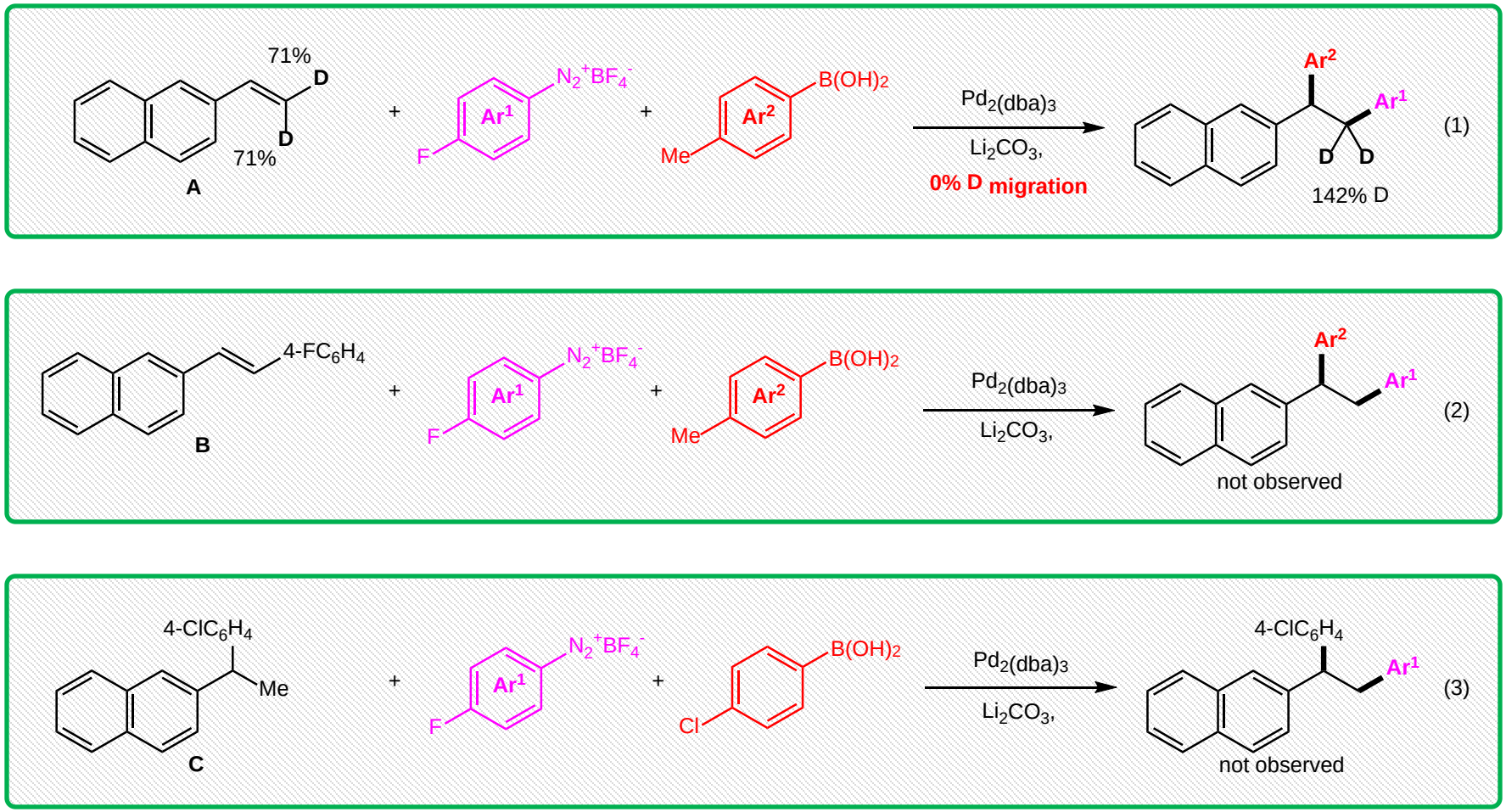


The scope of olefins

16 examples, 44-82% yields

Kuang, Z.; **Song, Q.** *et al. Org. Chem. Front.* **2017**, *4*, 1224.

Control Experiments



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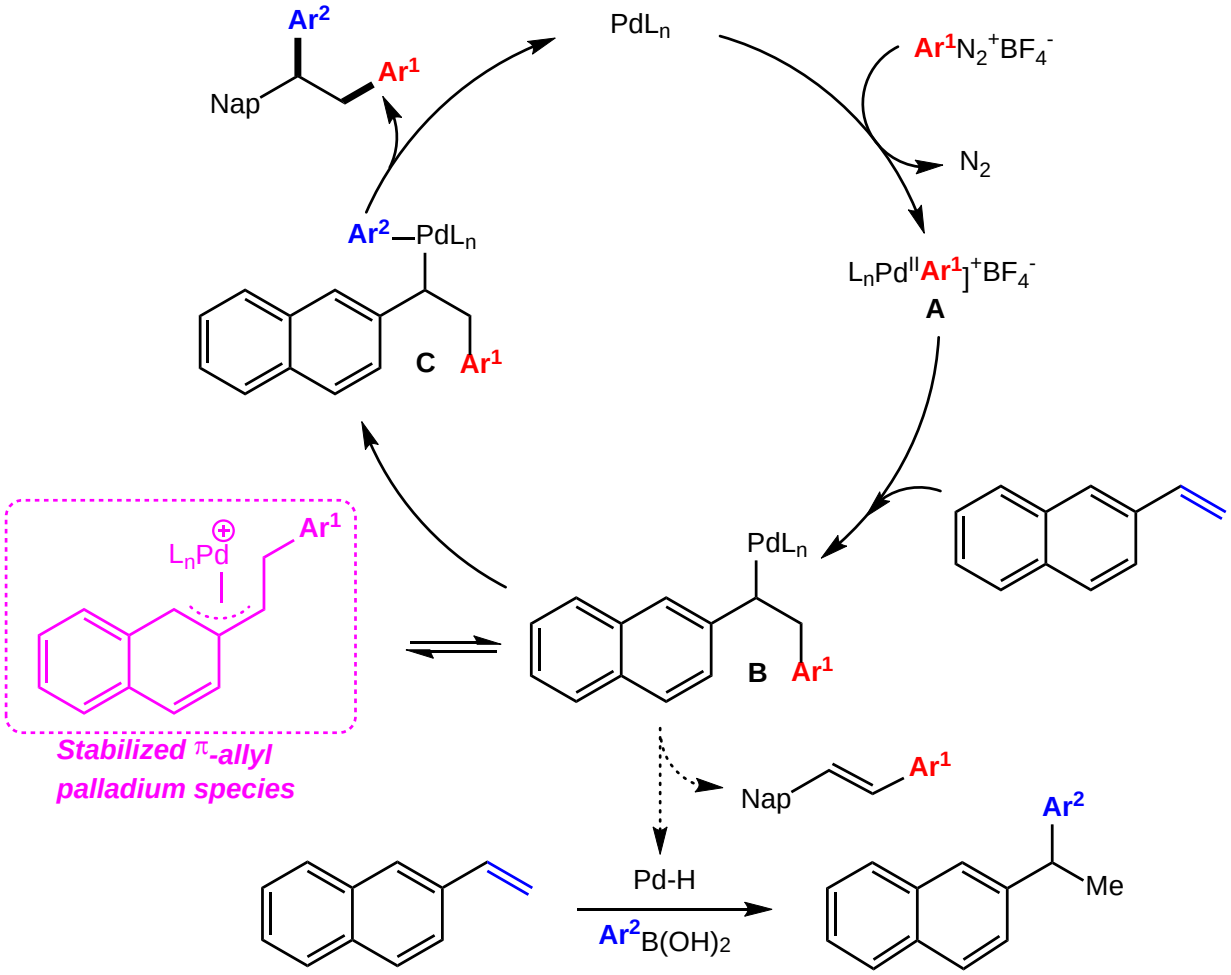
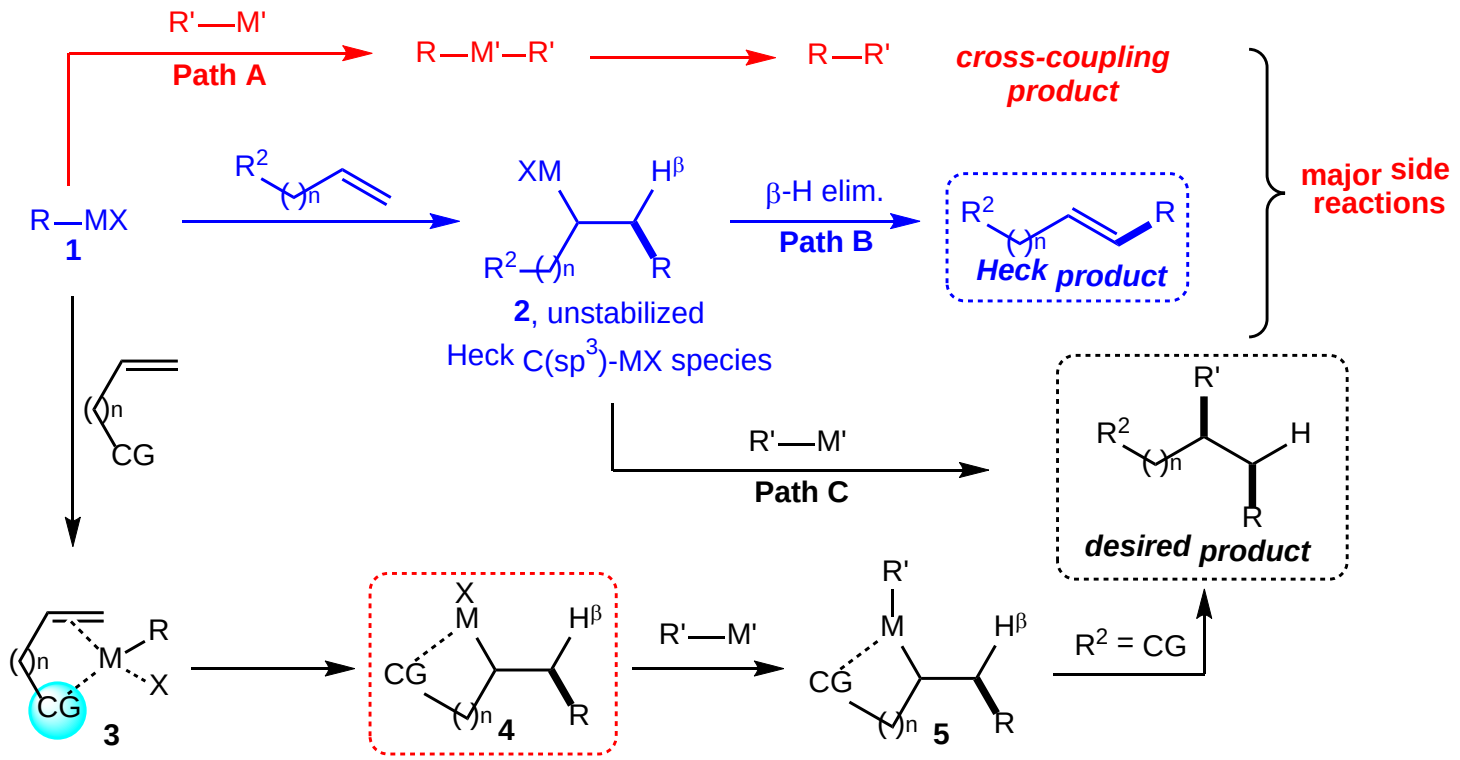
Possible Catalytic Cycle



Kuang, Z.; **Song, Q.** *et al. Org. Chem. Front.* **2017**, *4*, 1224.

Ni-catalyzed 1,2-Difunctionalization of Olefins

Strategy for Regioselective Olefin Dicarbofunctionalization

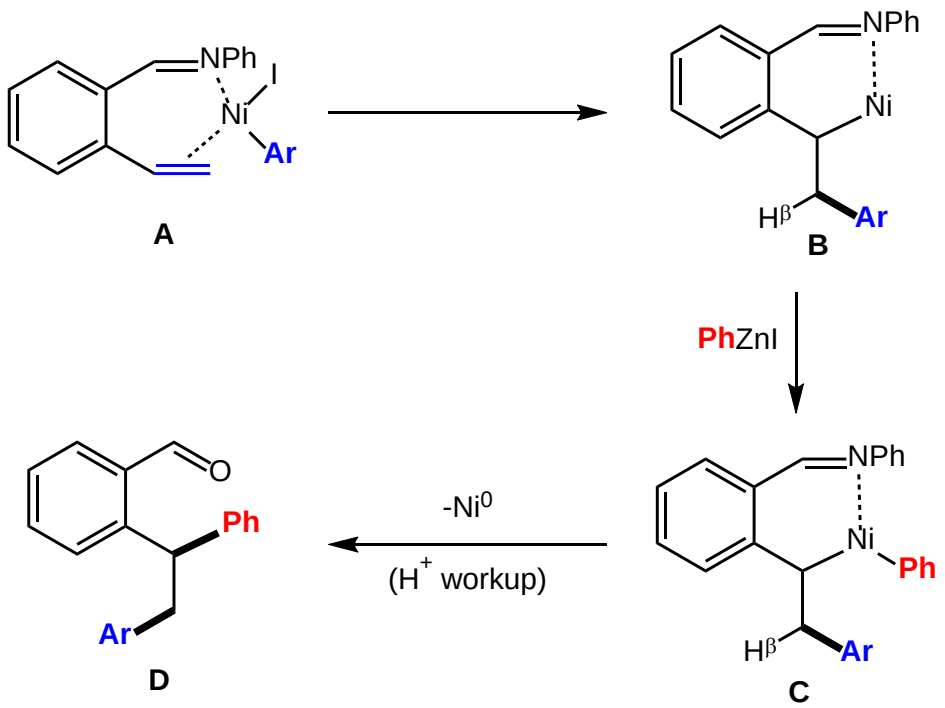


CG = coordinating group; M = transition metal; R'M' = $ArZnX$, $ArMgX$, $ArBR_2$

Shrestha, B.; **Giri, R.** *et al. J. Am. Chem. Soc.* **2017**, *139*, 10653.

Ni-catalyzed 1,2-Difunctionalization of Olefins

Pathway for Regioselective 1,2-Dicarbofunctionalization



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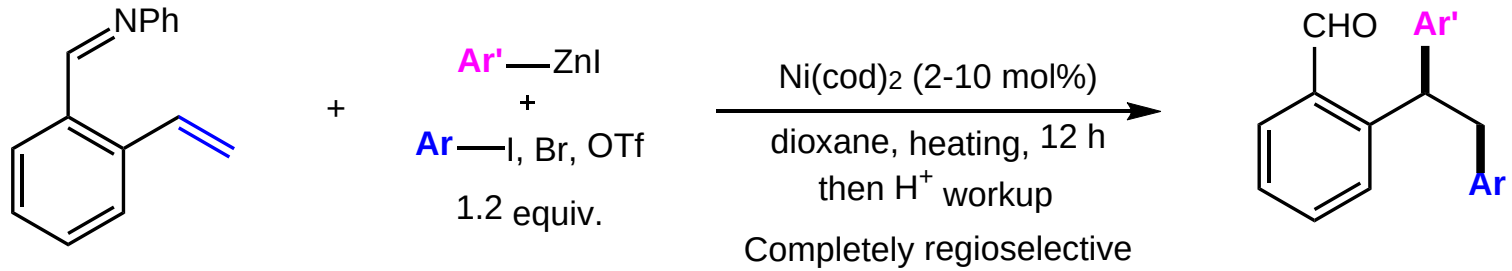
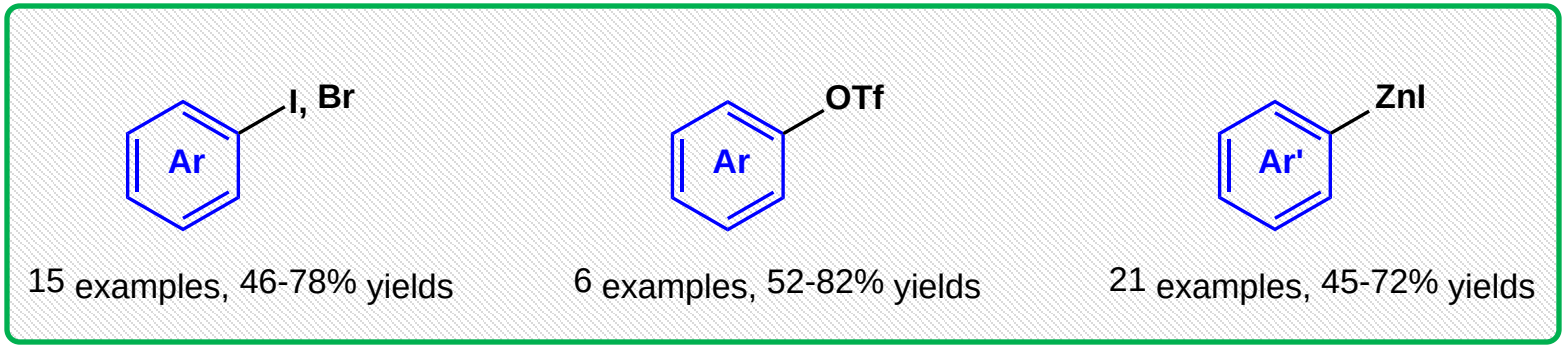
Ni-catalyzed 1,2-Difunctionalization of Olefins





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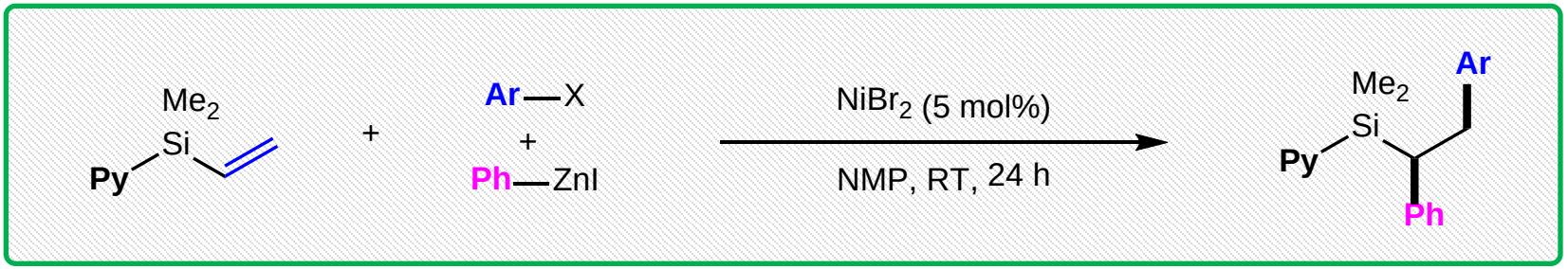
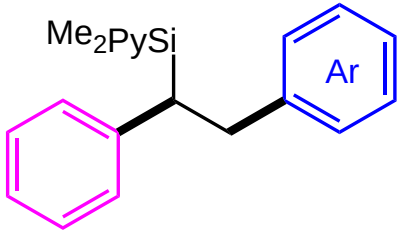
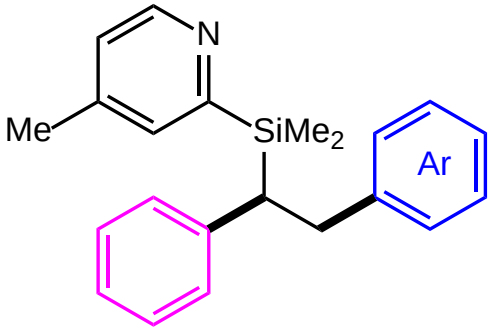
Pd-catalyzed Diarylation of Terminal Alkenes

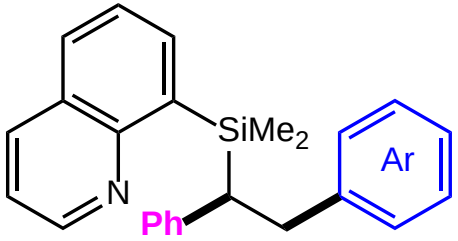




12 examples, 42-75% yields



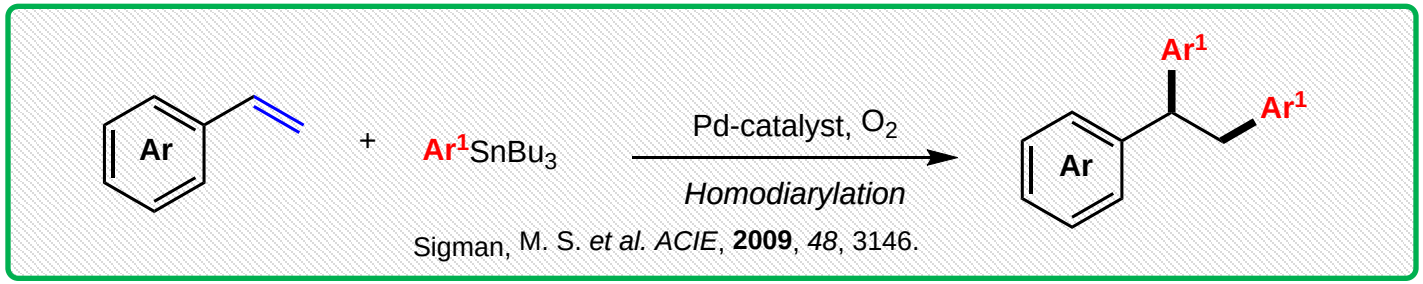
2 examples, 50% and 56% yields



2 examples, 52% and 54% yields

Thapa, S.; **Giri, R.** *et al. Chem. Sci.* **2018**, *9,* 904.

Ni-catalyzed Diarylation of Alkenylarenes



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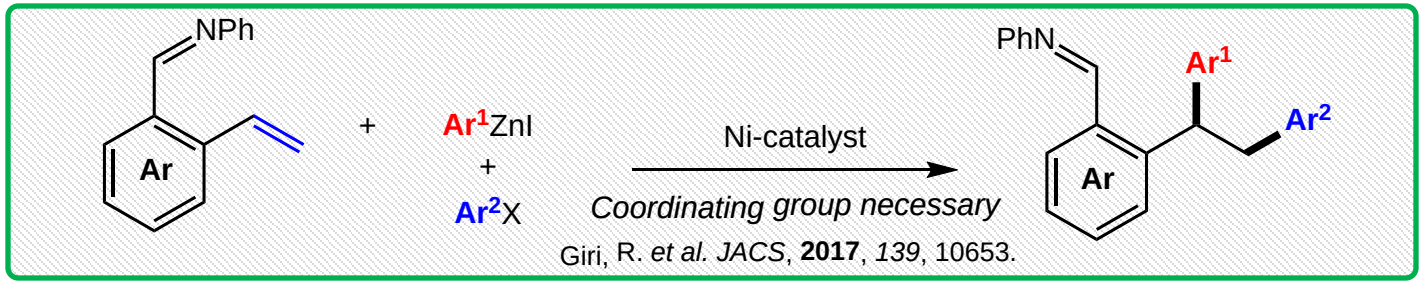

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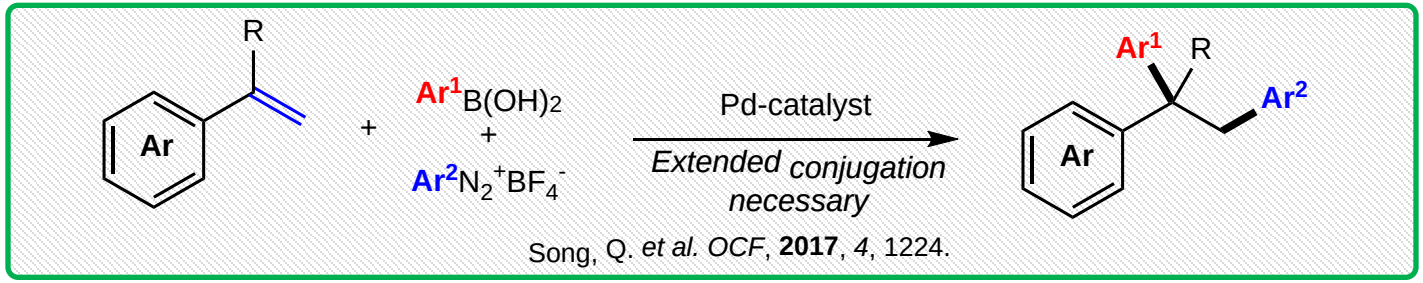

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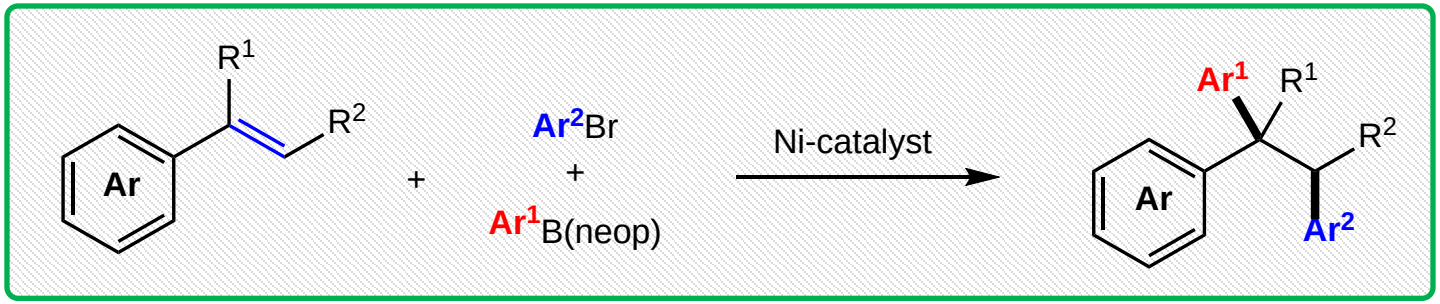
Ni-catalyzed Diarylation of Alkenylarenes

This work:



- ***Simple Ni^{II}-precatalyst***
- ***High diastereoselectivities***
- ***Alkenylarenes(mono-, 1,2-di, 1,1-di-substituted)***

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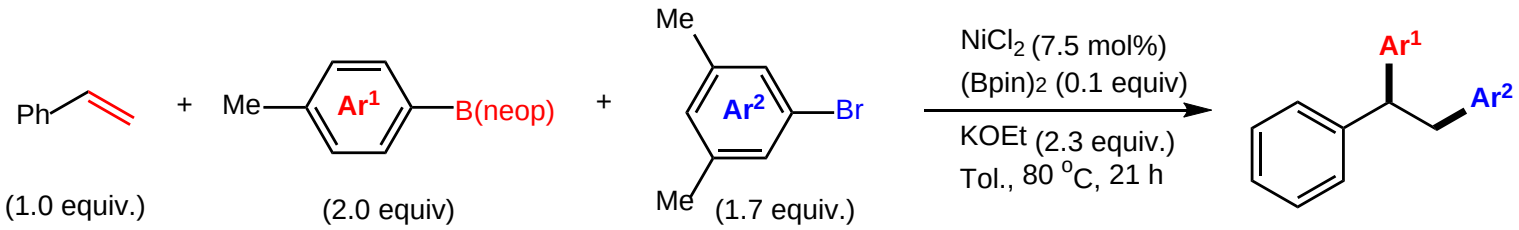
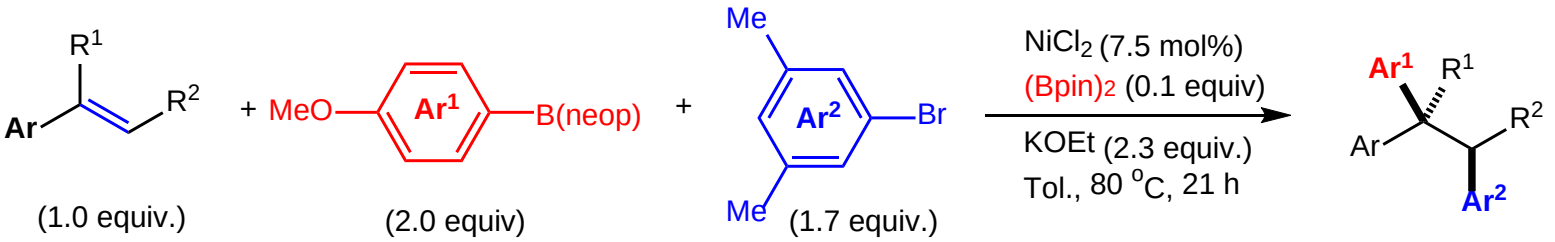
Change from Standard Conditions

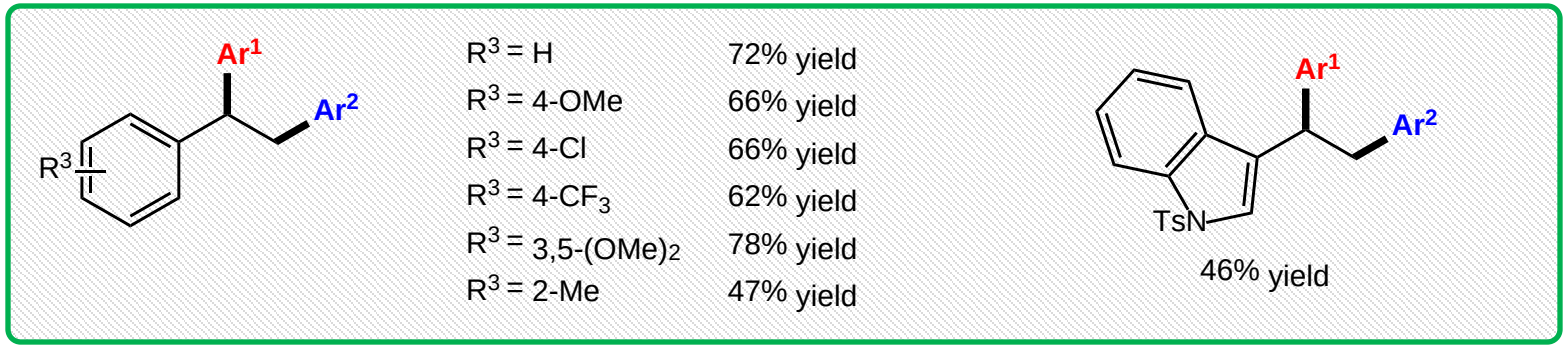


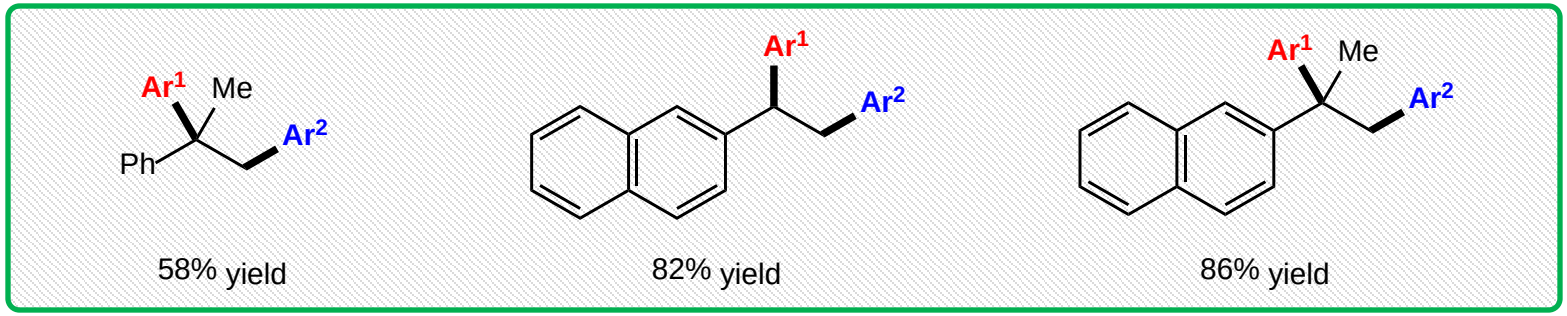
(1.0 equiv.) (2.0 equiv) (1.7 equiv.)

Entry	Change from Standard Conditions	Yield (%)
1	**no change**	**77**
2	No $(Bpin)_2$	< 2
3	0.1 equiv of $(Bneop)_2$ instead of 0.1 equiv of $(Bpin)_2$	70
4	1.0 equiv of Zn^0 or Mn^0 instead of 0.1 equiv of $(Bpin)_2$	< 2
5	$Ni(COD)_2$ instead of $NiCl_2$	54
6	$NiCl_2(PCy_3)_2$ instead of $NiCl_2$	< 2
7	$NiCl_2$(bpy) instead of $NiCl_2$	< 2
8	$NiCl_2$(DME) instead of $NiCl_2$	73
9	1.2 equiv of ArBr instead of 1.7 equiv of ArBr	68
10	1.8 equiv of ArB(neop) instead of 2.0 equiv of ArB(neop)	72
11	NaOEt instead of KOEt	16

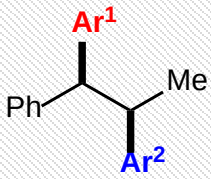
Evaluation of Various alkenes



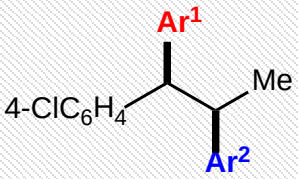




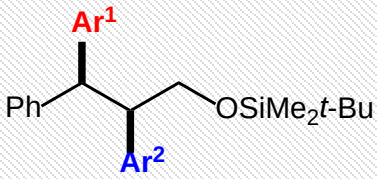
Evaluation of Various alkenes



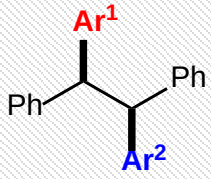
81% yield



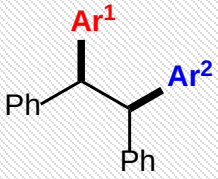
56% yield



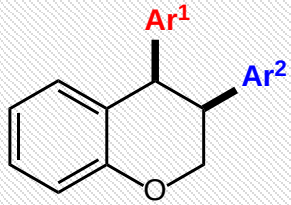
54% yield



85% yield, >20:1 dr
from *trans*-alkene

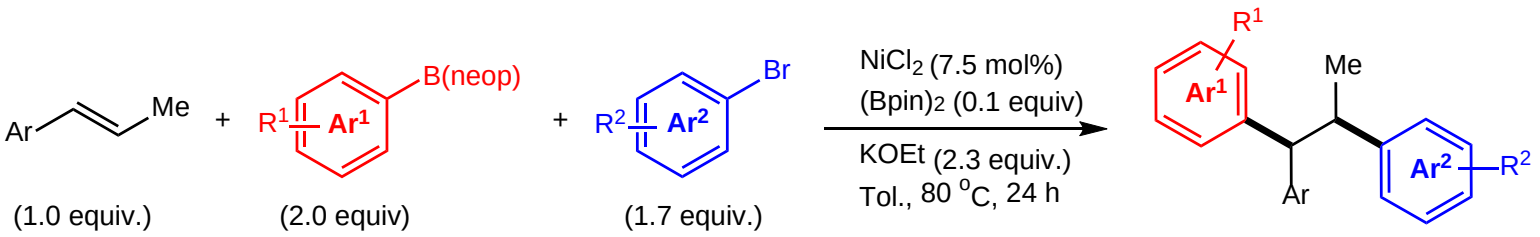


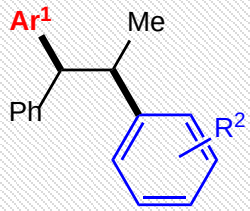
59% yield, 8:1 dr
from *cis*-alkene



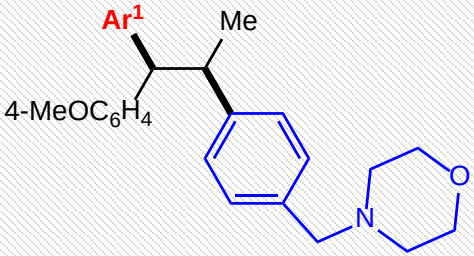
46% yield

Evaluation of ArBr



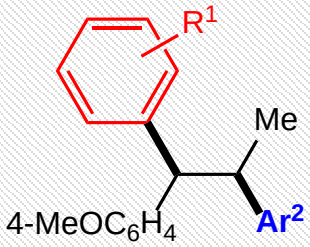


R^2 = H	79% yield
R^2 = 4-F	65% yield
R^2 = 4-NMeBoc	42% yield
R^2 = 4-pyrrolidine	65% yield
R^2 = 3,5-(t-Bu)$_2$	76% yield
R^2 = 2-CO_2Me	38% yield
R^2 = 2-Me	81% yield

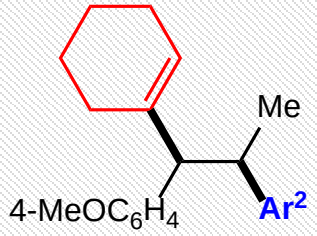


43% yield

Evaluation of ArB(neop)

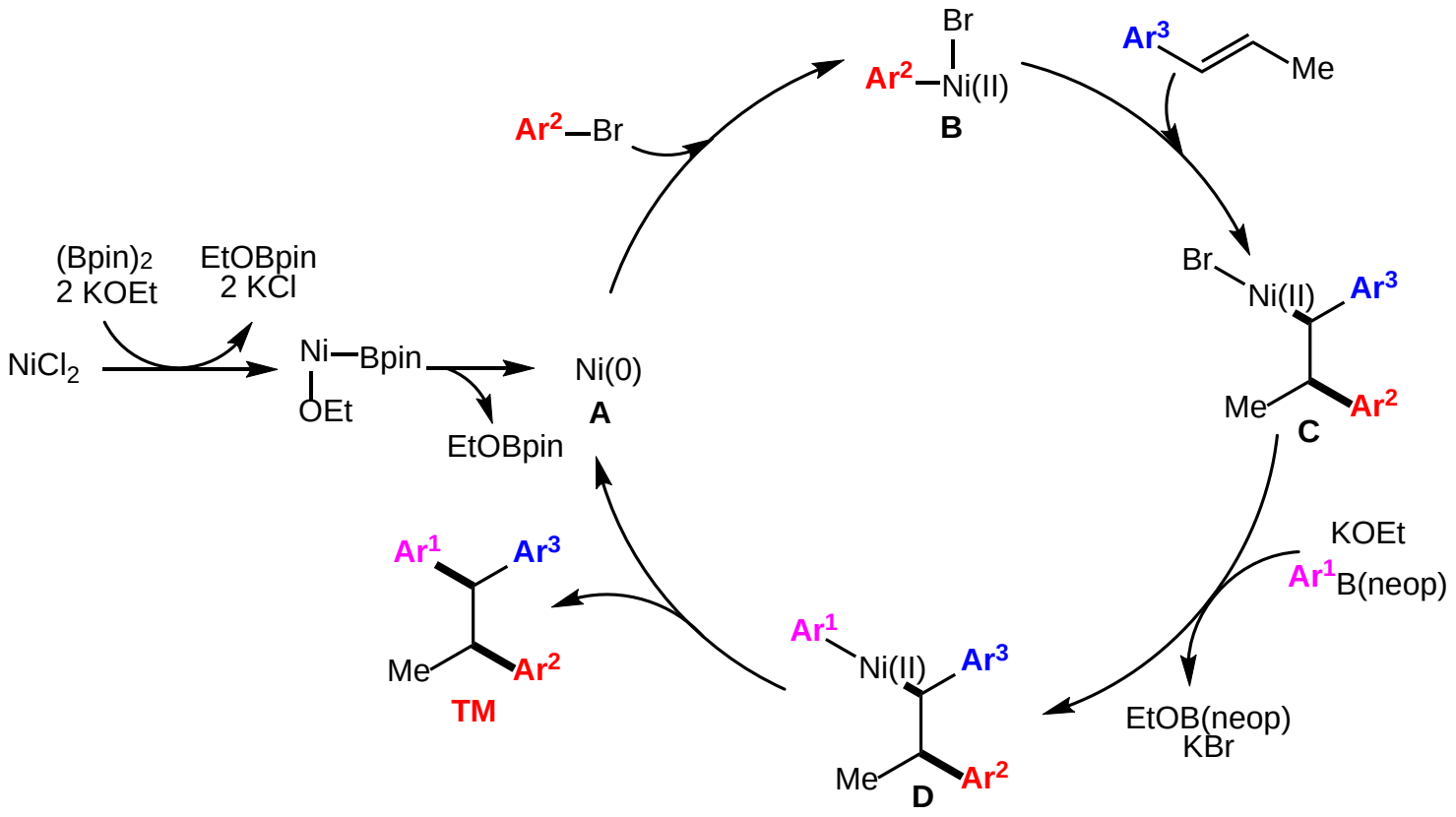


R^1 = H	86% yield
R^1 = 4-CF_3	56% yield
R^1 = 4-Cl	61% yield
R^1 = 4-Me	84% yield
R^1 = 4-OBn	80% yield
R^1 = 3-OMe	75% yield
R^1 = 3,5-(t-Bu)$_2$	77% yield



67% yield

Possible Catalytic Cycle



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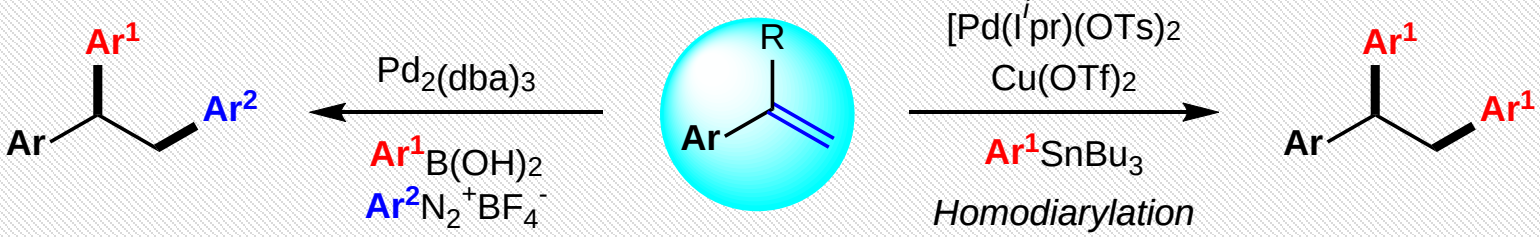
Summary

☐ Pd-catalyzed Diarylation of Alkenylarenes:



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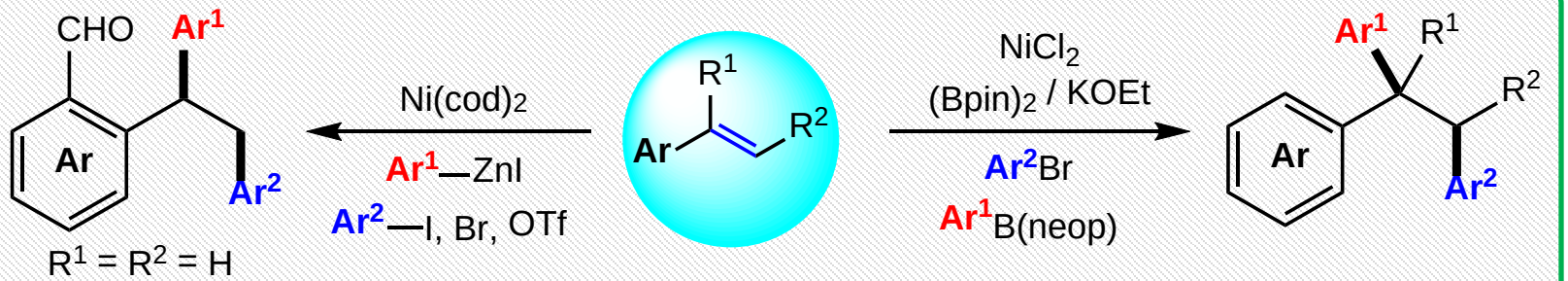
Sigman, M. S. *et al. ACIE*, **2009**, *48*, 3146.

☐ Ni-catalyzed Diarylation of Alkenylarenes:



Giri, R. *et al. JACS*, **2017**, *139*, 10653.

Brown, M. K. *et al. JACS*, **2018**, *140*, 10653.

The Structure of Introduction

烯烃在合成中的价值

↓

烯烃双官能化的意义

↓

烯烃双碳官能化现状

↓

烯烃双芳基化的现状

↓

该研究工作及其意义

The First Paragraph

Alkenes represent an appealing class of molecules for chemical synthesis because of their wide availability and ease of preparation. While alkene difunctionalization is known, reactions that incorporate two distinct carbon-based groups are more rare. In particular, addition of two different aryl groups across an alkene represents an attractive goal for method development because of the prevalence of polyarylalkanes in natural products and pharmaceutical agents.

The Structure of Last Paragraph

The Last Paragraph

In summary, a Ni-catalyzed diarylation of alkenylarenes has been developed. The method represents a substantial departure from known methods for reaction of vinylarenes in that specialized substrates are not required and the process is uniquely effective for diarylation of 1,2-disubstituted alkenylarenes. Such advances allow for the efficient and modular synthesis of a wide variety of polyarylalkanes.

Acknowledgement

Thanks

for your kind attention !