

Desulfitative C–C Cross-Coupling of Sulfonyl Chlorides and Sodium Arylsulfonates

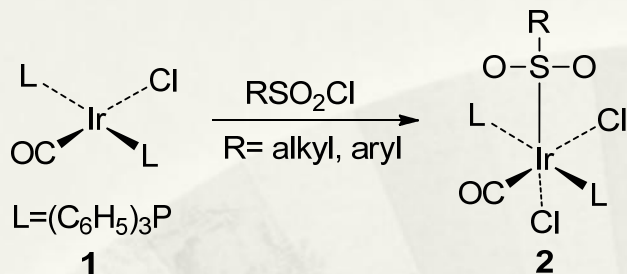
Reporter: Xinjin Li

Jun 23rd, 2014

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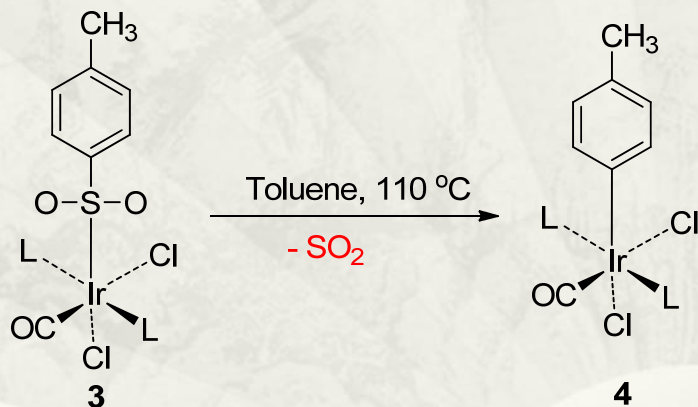
- * **Background**
- * **Desulfitative C–C Cross-Coupling of Sulfonyl Chlorides**
- * **Desulfitative C–C Cross-Coupling of Sodium Arylsulfonates**
- * **Summary and Perspective**

Background



Thermally stable

R= alkyl,
aryl: *p*-chlorophenyl,
p-nitrophenyl,
p-methoxyphenyl



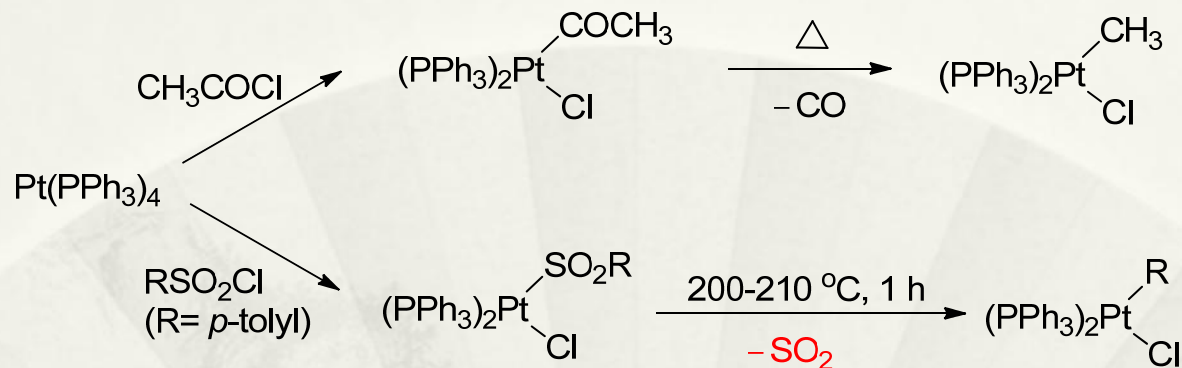
Infrared frequencies of **3**

SO_2 (asym) cm^{-1}	SO_2 (sym) cm^{-1}
1240, 1220	1065, 1055

The elimination of SO_2 represents the third gas (the other two: CO and N_2) forming elimination reaction whereby transition metal carbon bonds are formed.

James P. Collma, Warren R. Roper *J. Am. Chem. Soc.* **1966**, 88, 180-181

Background

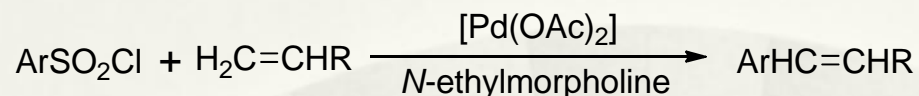


Infrared frequency of $(\text{PPh}_3)_2\text{Pt}(\text{SO}_2\text{R})\text{Cl}$ ($\text{R} = p\text{-tolyl}$)

SO_2 (asym) cm^{-1}	SO_2 (sym) cm^{-1}
1205	1043

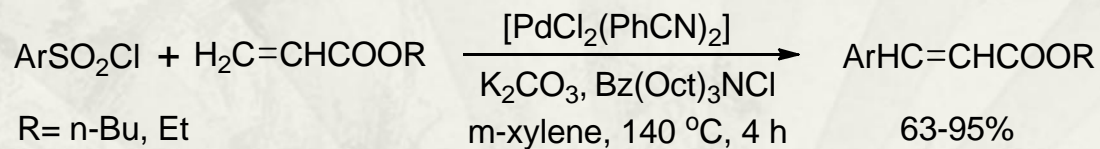
C. D. Cook and G. S. Jauhal, *Can. J. Chem.* **1967**, 46, 301-303

Desulfitative C–C Cross-Coupling of Arylsulfonyl Chlorides



A. Kasahara, T. Izumi, and et al. *Chem. Ind.* **1988**, 51-52

A. Kasahara, T. Izumi, and et al. *Chem. Ind.* **1989**, 192



PTC	GC-Yield (%)
Bz(Oct) ₃ NCl	95
Me(Oct) ₃ NCl	91
Bu ₄ NCl	36
	6

M. Miura, H. Hashimoto, and et al. *Tetrahedron Lett.* **1989**, 30, 975-976

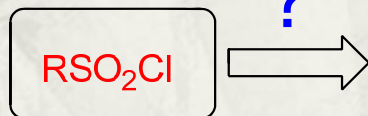
M. Miura, H. Hashimoto, and et al. *J. Chem. Soc. Perkin Trans.1* **1990**, 8, 2207-2211

Desulfitative C–C Cross-Coupling of Sulfonyl Chlorides



Pierre Vogel

University of Lausanne
(Switzerland)



C–C Cross-Coupling Reaction



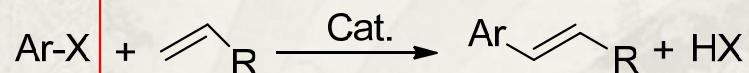
M = B : Suzuki-Miyaura

M = Sn : Stille

M = Si : Hiyama

M = Zn : Negishi

M = Mg: Kumada

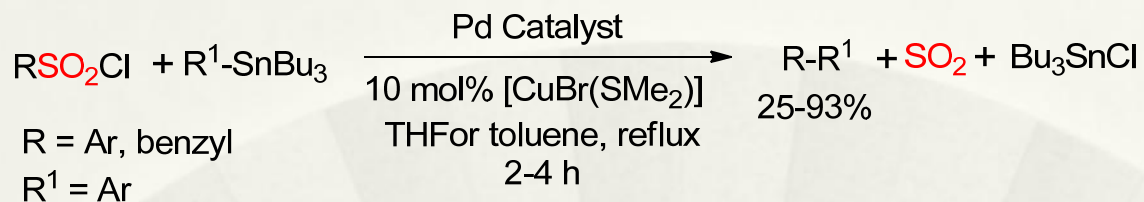


Mizoroki-Heck



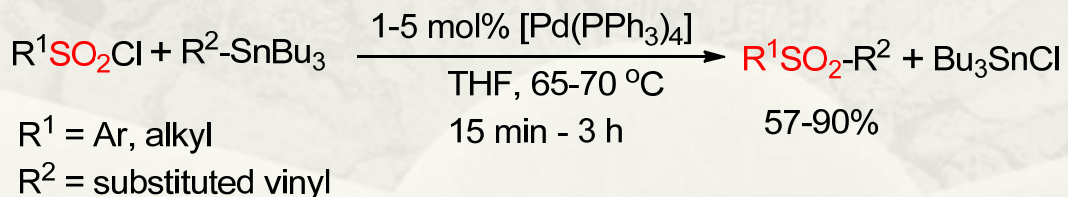
Sonogashira-Hagihara

Desulfitative Stille Cross-Couplings of Sulfonyl Chlorides



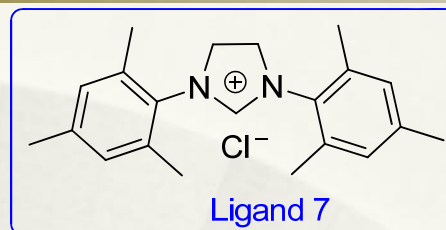
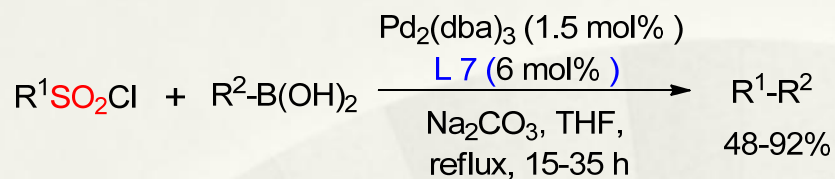
entry	Pd catalysts	yield (%)	by-product
1	1.5% Pd ₂ (dba) ₃ /5% TFP	90	
2	4% Pd ₂ (dba) ₃ /15% TFP	93	
3	8% Pd(PPh ₃) ₄	41	R ¹ -R ¹ , R-S-R

Srinivas Reddy Dubbaka and Pierre Vogel *J. Am. Chem. Soc.* **2003**, *125*, 15292-15293

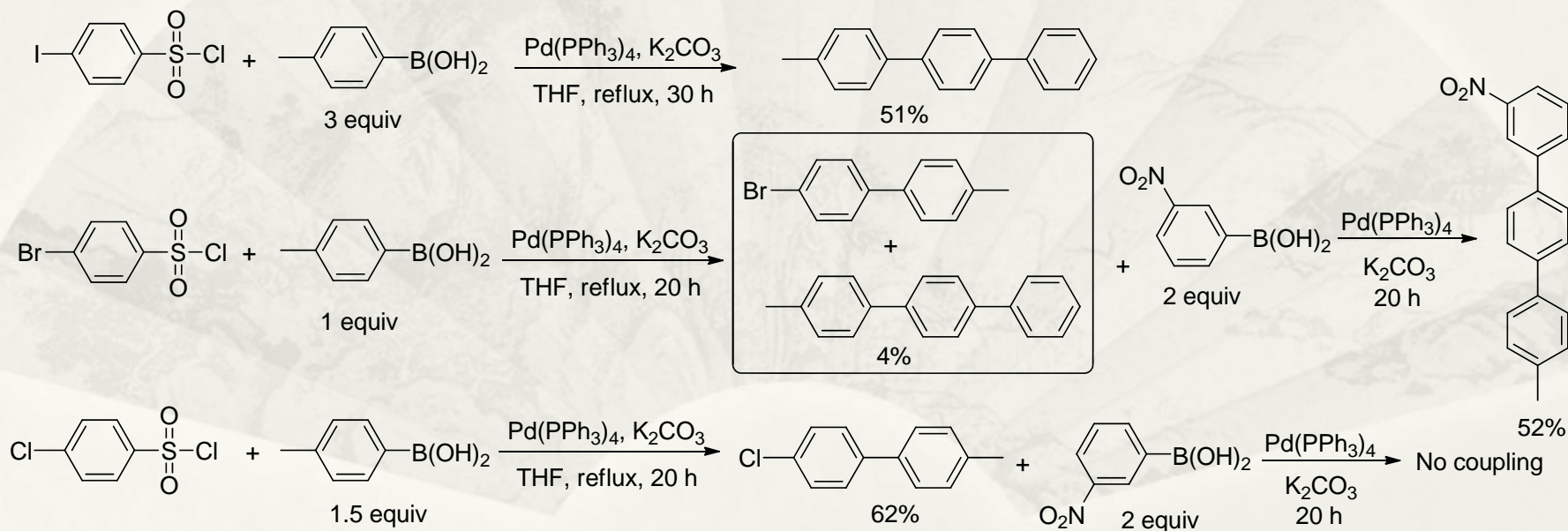


Sharada S. Labadie *J. Org. Chem.* **1989**, *54*, 2496-2498

Desulfitative Suzuki-Miyaura Cross-Couplings of Sulfonyl Chlorides

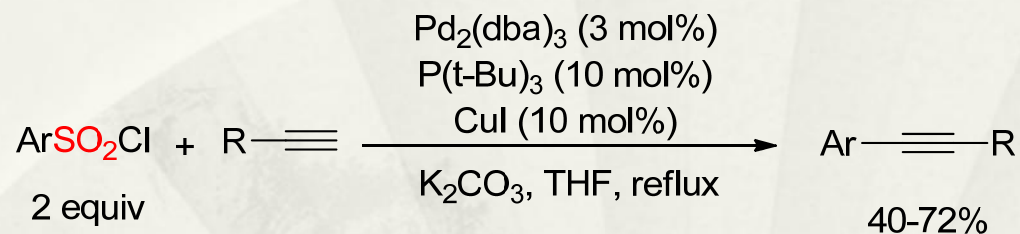


Reactivity Order for Suzuki-Miyaura Cross-Coupling Is $ArI > ArSO_2Cl > ArBr \gg ArCl$



Srinivas Reddy Dubbaka and Pierre Vogel *Org. Lett.* **2004**, *6*, 95-98

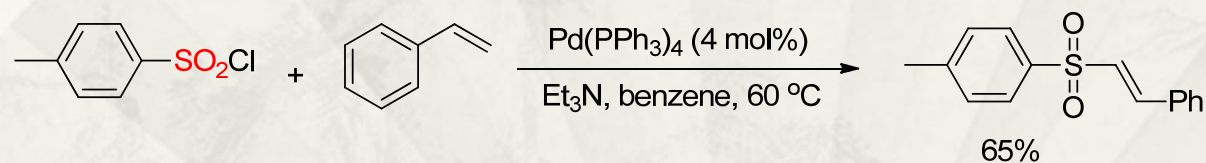
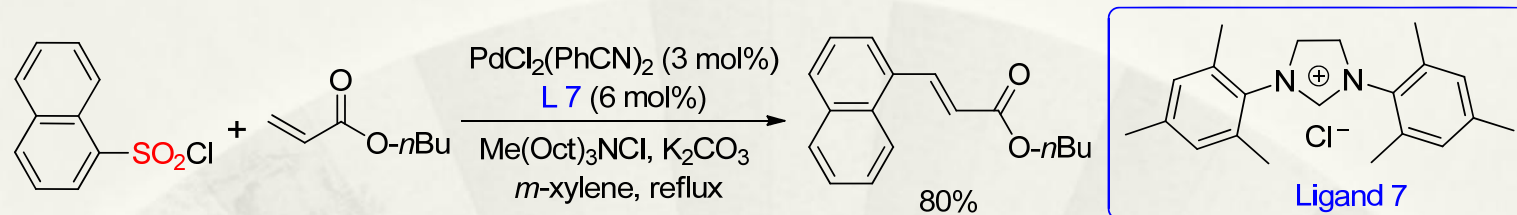
Desulfitative Sonogashira-Hagihara Cross-Couplings of Arylsulfonyl Chlorides



The homo-coupling of the alkynes can not be avoided !

Srinivas Reddy Dubbaka and Pierre Vogel *Adv. Synth. Catal.* **2004**, 346, 1793-1797

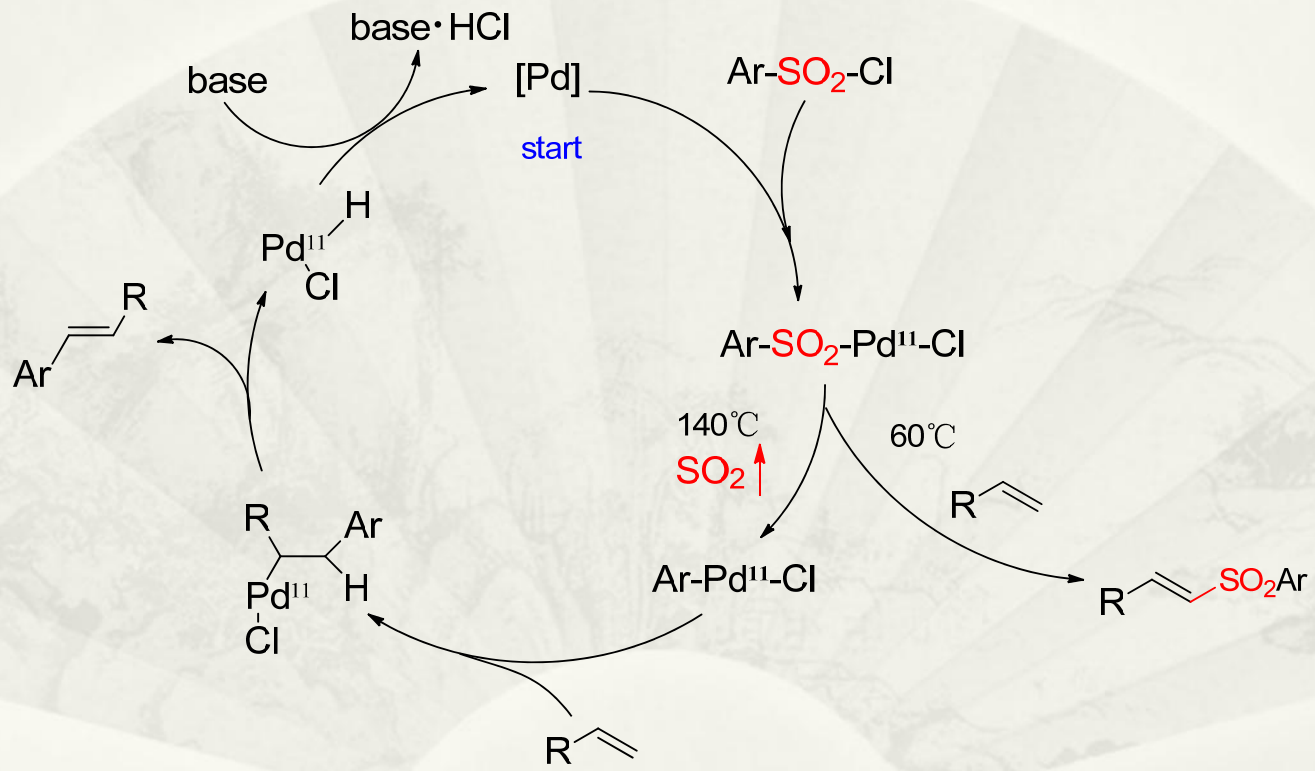
Desulfitative Mizoroki-Heck Cross-Couplings of Arylsulfonyl Chlorides



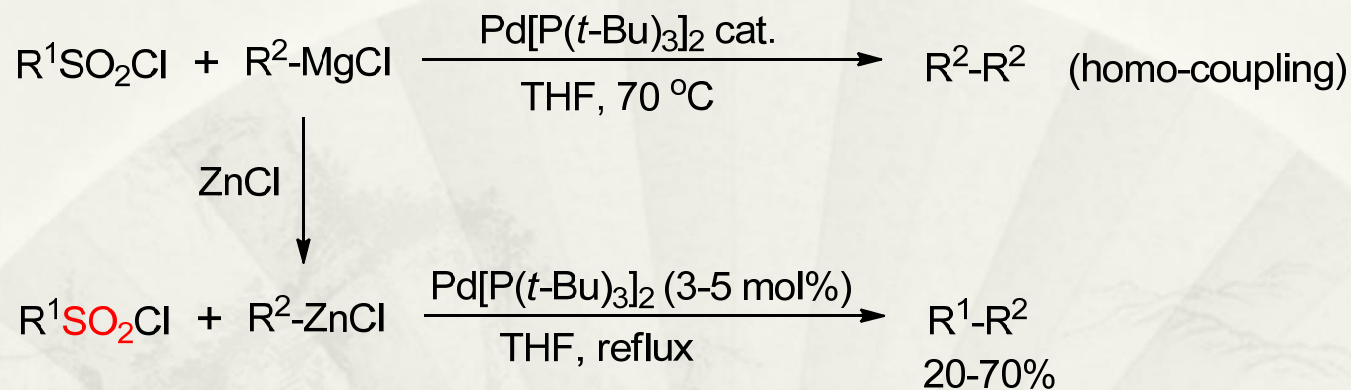
Srinivas Reddy Dubbaka and Pierre Vogel *Chem. Eur. J.* **2005**, *11*, 2633-2641

Desulfurative Mizoroki-Heck Cross-Couplings of Arylsulfonyl Chlorides

Proposed Mechanism



Desulfitative Negishi Cross-Couplings of Sulfonyl Chlorides

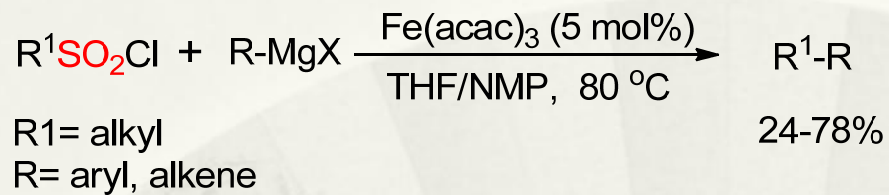


R¹ = 1-Hexyl

0

Srinivas Reddy Dubbaka and Pierre Vogel *Tetrahedron Lett.* **2006**, 47, 3345-3348

Iron-Catalyzed Desulfinylation of Sulfonyl Chlorides with Grignard Reagents



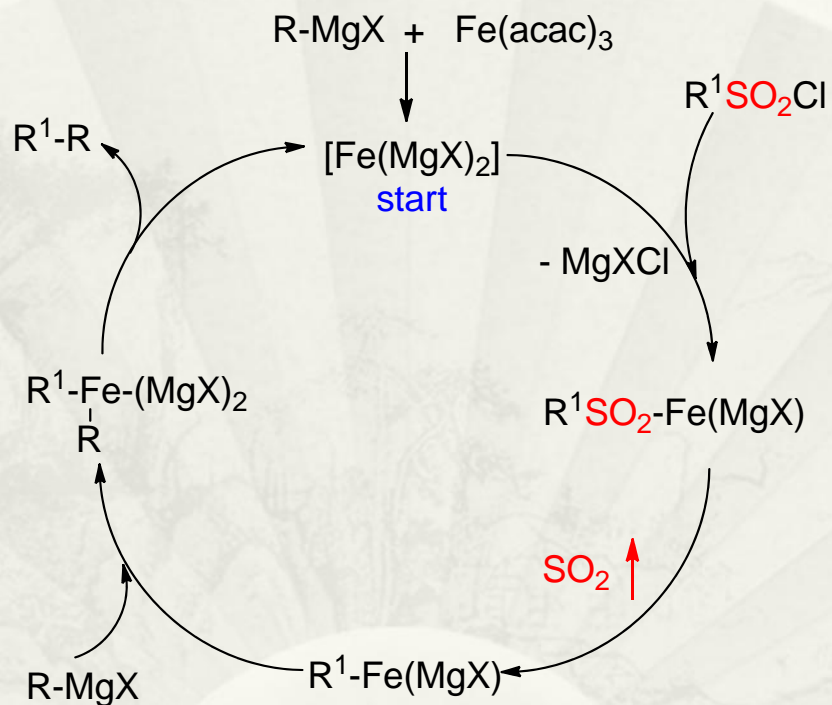
R¹= nOct, R= Ph

entry	conditions iron catalyst (equiv)	nOctPh (%)	nOctSO ₂ Ph (%)
1	no catalyst, 0°C to RT	–	76
2	Fe(acac)₃ (5 mol%), THF/NMP, 80 °C	72	–

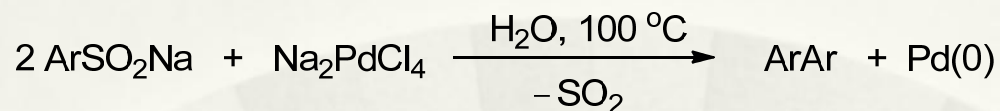
Srinivas Reddy Dubbaka and Pierre Vogel *Angew. Chem. Int. Ed.* **2008**, 47, 1305-1307

Iron-Catalyzed Desulfinylation of Sulfonyl Chlorides with Grignard Reagents

Proposed Mechanism

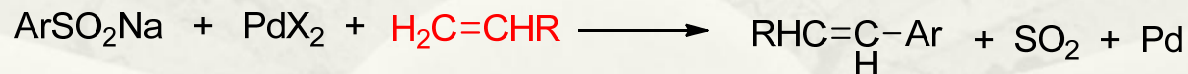


Desulfitative C–C Cross-Coupling of Sodium Arylsulfonates



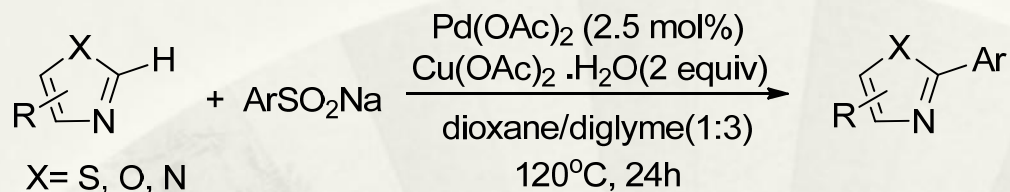
Ar	HgCl ₂ (mol %)	Yield (%)
Ph	0	35
Ph	10	71
<i>p</i> -tolyl	0	19
<i>p</i> -tolyl	10	63

Klaus Garves *J. Org. Chem.* **1970**, 35, 3273-3275

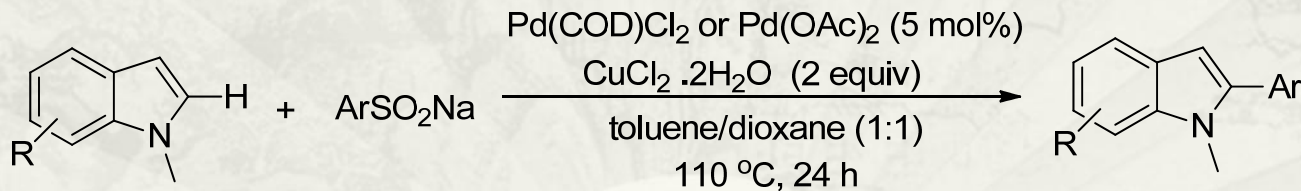


R. Selke, W. Thiele, *J. Prakt. Chem.* **1971**, 313, 875-880

C–H Arylation

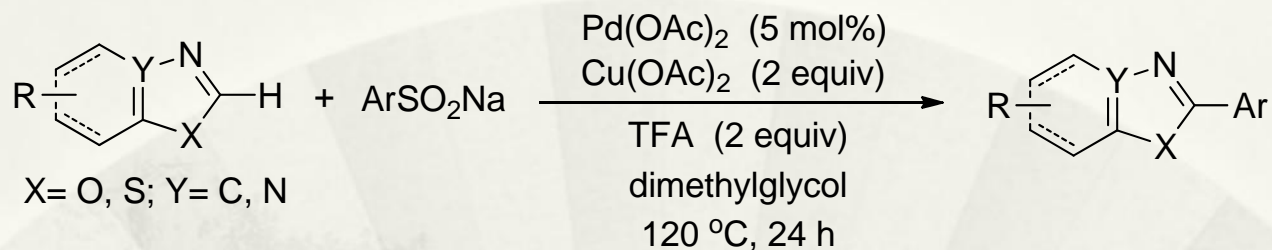


Ru Chen, Saiwen Liu, GuoJun Deng and et al. *Org. Biomol. Chem.*, **2011**, 9, 7675-7679

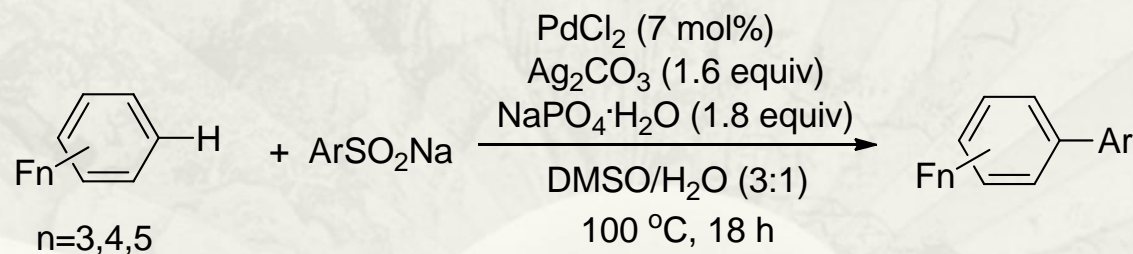


Mingyue Wu, HeAn Luo, GuoJun Deng and et al. *Adv. Synth. Catal.* **2012**, 354, 335-340

C-H Arylation



Min Wang, Dengke Li, Wei Zhou, Lei Wang *Tetrahedron* **2012**, 68, 1926-1930

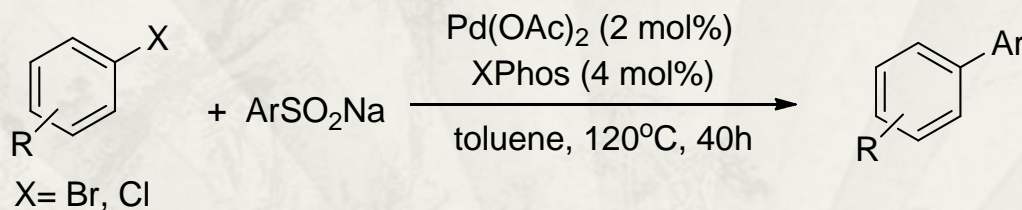


Tao Miao, Lei Wang *Adv. Synth. Catal.* **2014**, 356, 429-436

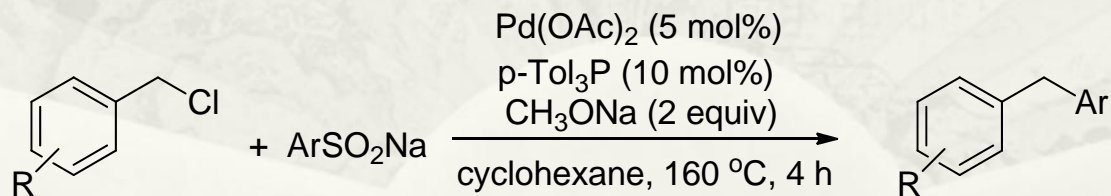
C–X Arylation



Dirk H. Ortgies, Pat Forgione and et al. *Synthesis* **2013**, 45, 694-702

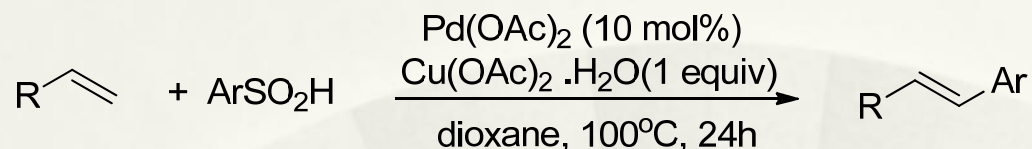


Chao Zhou, Yaming Li, Chunying Duan and et al. *Chin. J. Chem.* **2013**, 31, 1269-1273

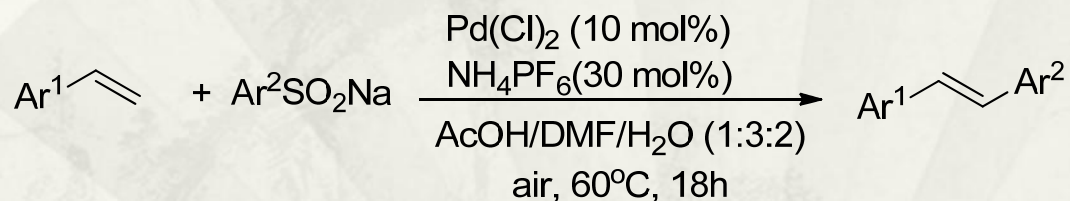


Feng Zhao, Qi Tan, GuoJun Deng and et al. *Org. Lett.*, **2013**, 15, 1520-1523

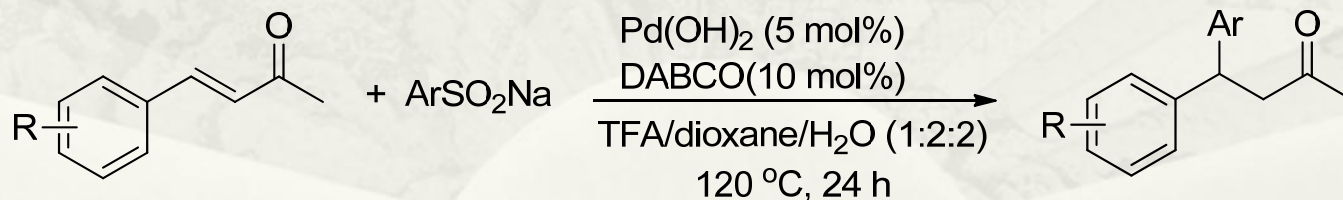
Arylation of alkenes



Guan-Wu Wang and Tao Miao *Chem. Eur. J.* **2011**, *17*, 5787- 5790

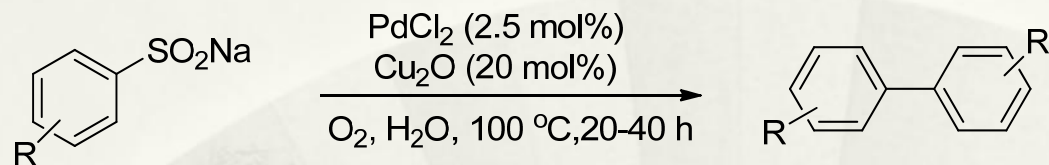


Nobukazu Taniguchi *Synlett.* **2013**, *9*, 2571-2574

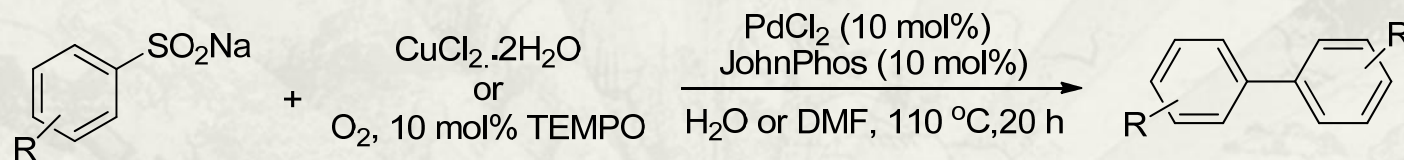


Wen Chen, Xianya Zhou, GuoJun Deng and et al. *Tetrahedron Lett* **2012**, *53*, 4347-4350

Desulfurative homo-coupling of Sodium Arylsulfinate



Bin Rao, Weixi Zhang, Lan Hu and Meiming Luo *Green Chem.*, **2012**, *14*, 3436-3440



Dirk H. Ortgies, Fei Chen, and Pat Forgione *Eur. J. Org. Chem* DOI: 10.1002/ejoc.201402134

Summary and Perspective

- * **Sulfonyl chlorides and sodium arylsulfonates, as versatile reagents, are extensively used for Desulfitative C–C Cross-Coupling reactions.**
- * **Desulfitative C-C Cross-Coupling reactions are commonly catalyzed by Palladium.**
- * **Exploring mild conditions will expand the application of these organosulfur compounds in Desulfitative Cross-Coupling reactions.**



Thanks for your attention!