

Fused pyridine derivatives

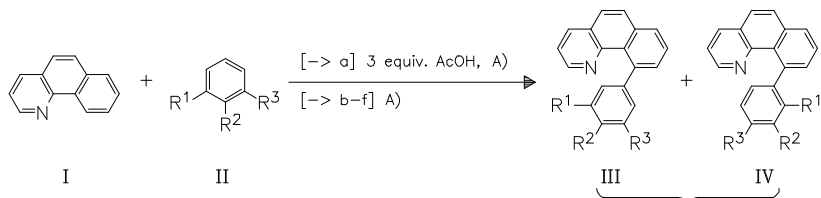
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DOI: 10.1002/chin.201131150

31- 150

Controlling Site Selectivity in Pd-Catalyzed Oxidative Cross-Coupling Reactions.

— This paper describes studies that address the factors controlling site selectivity in the Pd-mediated oxidative coupling of 1,3-disubstituted and 1,2,3-trisubstituted arenes. It is demonstrated, that with carboxylate X-type ligands, in the presence of quinone, and in the presence of acid, isomer (III) is formed selectively. Switching to carbonate as the X-type ligand at Pd reverses the selectivity to favor isomer (IV). — (LYONS, T. W.; HULL, K. L.; SANFORD, M. S.; J. Am. Chem. Soc. 133 (2011) 12, 4455-4464, <http://dx.doi.org/10.1021/ja1097918>; Dep. Chem., Univ. Mich., Ann Arbor, MI 48109, USA; Eng.) — Bartels



A): 1 equiv. benzoquinone, 4 equiv. DMSO
Pd(OAc)₂/benzoquinone (1:5) (cat.)
neat, 150°C, [15 h]

a R ¹ , R ³ : -O-iPr; R ² : -H	94% (GC, 15:1)
b R ¹ , R ³ : -Me; R ² : -NO ₂	100% (GC, 64:1)
c R ¹ , R ² : -Me; R ³ : -Cl	95% (GC, 60:1)
d R ¹ , R ² : -Me; R ³ : -O-Me	77% (GC, 53:1)
e R ¹ , R ² : -O-Me; R ³ : -H	89% (GC, 41:1)
f R ¹ , R ³ : -Me; R ² : -H	84% (GC, 55:1)

I $\xrightarrow[\text{B)}]{\text{(II)}}$ III + IV

a	85% (GC, 1:6)
b	69% (GC, 1:5)
c	67% (GC, 1:2)
d	67% (GC, 1:1)
e	91% (GC, 1:1)
f	69% (GC, 1:1)

B): 1 equiv. benzoquinone, 4 equiv. DMSO, 1 equiv. Cs₂CO₃, 50 mol% PdCl₂(benzoquinone)₂ (cat.)
neat, 150°C, [15 h]