Palladium-Catalyzed Completely Linear-Selective Negishi Cross-Coupling of Allylzinc Halides with Aryl and Vinyl Electrophiles

*Y. Yang, T. J. L. Mustard, P. H.-Y. Cheong,* S. L. Buchwald* (MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE AND OREGON STATE UNIVERSITY, CORVALLIS, USA)


**Significance:** Cheong, Buchwald, and co-workers report the first completely linear-selective palladium-catalyzed Negishi cross-coupling of various 3,3-disubstituted allylzinc reagents with (hetero)aryl and vinyl (pseudo)halides, leading to prenylated (hetero)aryl and alkenyl compounds in high yield and with excellent regioselectivity.

**Comment:** Apart from (hetero)aryl and vinyl bromides and chlorides, nonaflates and triflates were successfully used in this protocol. Computational studies reveal that an $\eta^1$-a reductive elimination is preferred due to energetic reasons, leading exclusively to the prenylated products. Thus, the choice of catalyst and transmetalation reagent is crucial.

---

Y. YANG, T. J. L. MUSTARD, P. H.-Y. CHEONG,* S. L. BUCHWALD* (MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE AND OREGON STATE UNIVERSITY, CORVALLIS, USA)

Palladium-Catalyzed Linear-Selective Negishi Cross-Coupling of Allylzinc Halides


**Selected examples:**

- 78% yield
  $\alpha/\gamma > 99:1$
  $X = Br, Y = Br$

- 93% yield
  $\alpha/\gamma > 99:1$
  $X = Br, Y = Br$

- 95% yield
  $\alpha/\gamma > 99:1$
  $X = Br, Y = Br$

- 94% yield
  $\alpha/\gamma > 99:1$
  $X = Br, Y = Br$

- 90% yield
  $\alpha/\gamma > 99:1$
  $X = OTf, Y = Br$

- 92% yield
  $\alpha/\gamma > 99:1$
  $X = ONf, Y = Br$

- 92% yield
  $\alpha/\gamma > 99:1$
  $E/Z = 84:16$
  $X = Br, Y = Br$

- 75% yield
  $\alpha/\gamma > 99:1$
  $E/Z > 99:1$
  $X = OTf, Y = OP(O)(OEt)$_2

---

SYNFACTS Contributors: Paul Knochel, Nadja M. Barl

SYNFACTS 2014, 10(3), 0297 Published online: 17.02.2014

DOI: 10.1055/s-0033-1340750; Reg-No.: P00314SF