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


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

**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 \( \eta^1-\alpha \) reductive elimination is preferred due to energetic reasons, leading exclusively to the prenylated products. Thus, the choice of catalyst and transmetalation reagent is crucial.

**Selected examples:**

- **78% yield**
  - \( \omega/\gamma > 99:1 \)
  - \( X = \text{Br, Cl} \), \( Y = \text{Br} \)

- **93% yield**
  - \( \omega/\gamma > 99:1 \)
  - \( X = \text{Br, Cl} \), \( Y = \text{Br} \)

- **95% yield**
  - \( \omega/\gamma > 99:1 \)
  - \( X = \text{Br, Cl} \), \( Y = \text{Br} \)

- **94% yield**
  - \( \omega/\gamma > 99:1 \)
  - \( X = \text{Br, Cl} \), \( Y = \text{Br} \)

- **90% yield**
  - \( \omega/\gamma > 99:1 \)
  - \( X = \text{OTf} \), \( Y = \text{Br} \)

- **92% yield**
  - \( \omega/\gamma > 99:1 \)
  - \( X = \text{ONf} \), \( Y = \text{Br} \)

- **75% yield**
  - \( \omega/\gamma > 99:1 \)
  - \( E/Z > 99:1 \)
  - \( X = \text{OTf} \), \( Y = \text{OP(O)(OEt)}_2 \)