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 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
  \( \omega/\gamma > 99:1 \)
  \( X = \text{Br}, Y = \text{Br} \)

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

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

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

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

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

- 92% yield
  \( \omega/\gamma > 99:1 \)
  \( E/Z = 84:16 \)
  \( X = \text{Br}, Y = \text{Br} \)

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