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
  \[ \text{X} = \text{Br}, \text{Y} = \text{Br} \]
  \[ \alpha/\gamma > 99:1 \]

- 93% yield
  \[ \text{X} = \text{Br}, \text{Y} = \text{Br} \]
  \[ \alpha/\gamma = 99:1 \]

- 95% yield
  \[ \text{X} = \text{Br}, \text{Y} = \text{Br} \]
  \[ \alpha/\gamma > 99:1 \]

- 94% yield
  \[ \text{X} = \text{Br}, \text{Y} = \text{Br} \]
  \[ \alpha/\gamma > 99:1 \]

- 90% yield
  \[ \text{X} = \text{OTf}, \text{Y} = \text{Br} \]
  \[ \alpha/\gamma > 99:1 \]

- 92% yield
  \[ \text{X} = \text{Br}, \text{Y} = \text{Br} \]
  \[ \alpha/\gamma > 99:1 \]

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

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