Palladium-Catalyzed Cross-Coupling of 1,1-Diboronates

**Significance:** The authors demonstrate a palladium(0)-catalyzed reaction of 1,1-diboronates with substituted vinyl bromides or dibromoalkenes to give 1,4-dienes or allenes in good yields while showing good functional group tolerance.

**Comment:** When using 1,1-dibromoalkenes bearing a terminal alkynyl group as the substrate, the palladium(0)-catalyzed coupling described above can be followed by a CuI-catalyzed allenation with N-tosylhydrazones to give unsymmetrical diallenes.

**Equation:**

\[
\text{R}^1\text{Br} + \text{Bpin} \text{R}^2 \xrightarrow{[\text{Pd}(\text{P}^\text{t}-\text{Bu}_3)\text{}_2]} \text{LiOH} \xrightarrow{1,4\text{-dioxane-H}_2\text{O}} 25^\circ\text{C}, 1-12\text{ h} \]

 up to 94% yield

**Selected examples:**

- **R**\(^1\) = Ar, Alk
  - **R**\(^2\) = CH\(_2\)Bn, i-Pr, Cy
  - 45% yield, E/Z > 20:1
  - 57% yield, E/Z > 20:1
  - 80% yield, E/Z = 11:1

**Equation:**

\[
\text{R}^1\text{Br} + \text{Bpin} \text{R}^2 \xrightarrow{[\text{Pd}(\text{PPh}_3)_4]} \text{CsOH} \xrightarrow{1,4\text{-dioxane-H}_2\text{O}} 25^\circ\text{C}, 12-24\text{ h} \]

 up to 79% yield

**Selected examples:**

- **R**\(^1\) = Ar, Alk
  - **R**\(^2\) = CH\(_2\)Bn, Alk, Cy
  - 74% yield
  - 79% yield
  - 76% yield