Pd-Ligand Controlled Cyclization for the Preparation of Heteroaromatics

**Significance:** Various vinyl diphenylamine intermediates are selectively cyclized to the corresponding five-, six- or seven-membered heteroaromatics. The regioselectivity of these palladium-catalyzed cyclizations is almost exclusively directed by the used ligand.

**Comment:** By using 2-bromostyrene and 2-chloroaniline derivatives in this palladium-catalyzed reaction with DavePhos as ligand, a direct one-pot synthesis was achieved, furnishing 5H-diazepines in good to excellent yields.

**Selected examples:**

- Synthesis of dibenzazepines:
  - 7-endo 99% yield
  - Synthesis of carbazoles:
    - Pd(dba)₂ (0.75 mol%) NaOt-Bu (1.5 equiv) 1,4-dioxane, 110 °C
  - Synthesis of indoles:
    - Pd(dba)₂ (0.75 mol%) NaOt-Bu (1.5 equiv) 1,4-dioxane, 110 °C
  - Synthesis of acridines:
    - P(r-Bu)₂ (7.5 mol%) NaOt-Bu (1.5 equiv) PhMe, 100 °C
  - Synthesis of indoles:
    - Pd(OAc)₂ (10 mol%) Cu(OAc)₂ (1.5 equiv) DMF, AcOH 100 °C, 12 h
  - Synthesis of dibenzazepines:
    - NaOt-Bu (1.5 equiv) 1,4-dioxane, 110 °C
  - Synthesis of carbazoles:
    - Pd(dba)₂ (0.75 mol%) NaOt-Bu (1.5 equiv) 1,4-dioxane, 110 °C
  - Synthesis of acridines:
    - P(r-Bu)₂ (7.5 mol%) NaOt-Bu (1.5 equiv) PhMe, 100 °C
  - Synthesis of indoles:
    - Pd(OAc)₂ (10 mol%) Cu(OAc)₂ (1.5 equiv) DMF, AcOH 100 °C, 12 h
  - Synthesis of dibenzazepines:
    - NaOt-Bu (1.5 equiv) 1,4-dioxane, 110 °C
  - Synthesis of carbazoles:
    - Pd(dba)₂ (0.75 mol%) NaOt-Bu (1.5 equiv) 1,4-dioxane, 110 °C
  - Synthesis of acridines:
    - P(r-Bu)₂ (7.5 mol%) NaOt-Bu (1.5 equiv) PhMe, 100 °C
  - Synthesis of indoles:
    - Pd(OAc)₂ (10 mol%) Cu(OAc)₂ (1.5 equiv) DMF, AcOH 100 °C, 12 h