Dihydrobenzofuran Synthesis by Palladium/Norbornene Cooperative Catalysis

**Significance:** This method builds on a previously developed palladium/norbornene-catalyzed Catellani reaction, extending its reactivity to include epoxides as substrate to access dihydrobenzofurans. Modification of the catalytic system by the use of bulky phosphine ligands and polar aprotic solvents promoted the coupling of epoxides, and tuning of the norbornene improved conversion by avoiding the formation of a norbornene-insertion byproduct. This reaction also demonstrated stereoretention when chiral epoxides were employed.

**Comment:** This extension of the Catellani reaction provides a convenient method to access functionalized dihydrobenzofurans. One notable feature of this reaction is the ability to use easily accessed chiral epoxides to produce dihydrobenzofurans with high enantiomeric excesses. Typical to the Catellani reactions, aryl iodides bearing 2-alkyl substituents were employed. Further development of this chemistry to avoid the necessity for the alkyl group or to expand the range of suitable 2-substituents might broaden the applicability of this method.

**Selected examples:**

- ![Example 1](image1)
  - 72% yield (5 mol% cat)
- ![Example 2](image2)
  - 90% yield
- ![Example 3](image3)
  - 46% yield, 99% ee
- ![Example 4](image4)
  - 65% yield
- ![Example 5](image5)
  - 73% yield
- ![Example 6](image6)
  - 86% yield
- ![Example 7](image7)
  - 55% yield
- ![Example 8](image8)
  - 99% ee

**RuPhos-Pd-G4 (10 mol%)**

**(±) NBE-1 (20 mol%)**

**NaOAc (150 mol%)**

**DMF (0.1 M), 120 °C**

44–99% yield

**Key words**

- dihydrobenzofurans
- cooperative catalysis
- aryl iodides
- epoxides
- palladium catalysis
- norbornene