Nickel-Catalyzed Enantioselective Synthesis of Benzobicyclo[2.2.2]octenes

**Significance:** The first catalytic asymmetric strategy toward the synthesis of benzobicyclo[2.2.2]-octenes from achiral substrates is reported. Derivatives of these products are known to exhibit biological activities. Alternatively, the benzobicyclo[2.2.2]octene 1 could undergo Bayer–Villiger oxidation and saponification to afford cis-substituted hydroxycarboxylic acid 2.

**Comment:** Following the authors’ initial report on the achiral variant of this reaction (Chem. Commun. 2006, 4599), the notable switch of Cy3P to a chiral phosphoramidite ligand L in this report conferred high enantioselectivities. The proposed catalytic cycle involves an enantiodiscriminating oxidative cyclization step followed by β-carbon elimination.