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Atom- and Step-Economical Pathway to Chiral Benzobicyclo[2.2.2]octenones through Carbon–Carbon Bond Cleavage

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Nickel-Catalyzed Enantioselective Synthesis of Benzobicyclo[2.2.2]octenes

$$\begin{array}{c} R^2 \\ R^2 \\ R^2 \\ R^3 \\ R^4 \\ R^5 \\$$

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**.

SYNFACTS Contributors: Mark Lautens, Lei Zhang Synfacts 2012, 8(5), 0513 Published online: 18.04.2012 **DOI:** 10.1055/s-0031-1290909; **Reg-No.:** L03812SF

Comment: Following the authors' initial report on the achiral variant of this reaction (*Chem. Commun.* **2006**, 4599), the notable switch of Cy_3P 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.