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**Rh-Catalyzed Synthesis of Benzooxapinones and Benzothiapinones**

**Significance:** Reported is the Rh-catalyzed synthesis of medium-ring heterocycles 2 and 4 via an intramolecular olefin hydroacylation of salicylaldehyde derivatives 1 and 3. Using (R,R)-Me-DuPHOS as the ligand leads preferentially to the 7-membered α-substituted products (>15:1 selectivity). However, 8-membered thioether 5 may be formed selectively in 91% yield using (S,S)-BDDP as ligand. The reaction tolerates electron-rich and electron-deficient substrates with equal efficiency, with excellent yields and enantioselectivities obtained in all cases. The authors also report mechanistic and deuterium-labeling studies, which confirm that heteroatom (O,S) coordination is crucial for the reaction to proceed (no product was observed when S was replaced by CH2), and that, in contrast to a previous report, reductive elimination is unlikely to be turnover-limiting (see: M. Brookhart and co-workers J. Am. Chem. Soc. 2007, 129, 2082).

**Comment:** The synthesis of medium-sized ring systems has often proved a considerable challenge. Although the advent of transition metal catalysis has allowed the rapid and efficient synthesis of medium-ring systems (see Review below), the development of efficient enantioselective syntheses has remained elusive. The current method is high-yielding and highly enantioselective, but relies on a heteroatom linker to promote coordination to Rh and eliminate formation of unwanted by-products. Products bearing either α- or β-stereogenic centers may be produced from a single substrate simply by changing the ligand used in the reaction, making this a flexible approach to enantioenriched medium-ring heterocycles.

**Review:** L. Yet Chem. Rev. 2000, 100, 2963-3008.