Tetrahydrofuroindoles by a Palladium-Catalyzed Asymmetric Dearomatization

**Significance:** The authors developed a palladium-catalyzed diastereoselective and enantioselective dearomatization for the synthesis of tetrahydrofuroindoles. Remarkably, the polarity of the solvent was found to play a key role in the diastereoselectivity. Compared with toluene, the reactions in acetonitrile occurred faster and produced the reversed diastereoisomer with higher enantioselectivity.

**Comment:** Mechanistic studies were conducted to illustrate the origin of the diastereodivergency. The kinetic experiments indicate that the reactions in different solvents proceed by the same pathway with different rate-limiting steps, thereby leading to a reversed stereocontrol. ESI-MS experiments support the existence of key palladium complex intermediates and the proposed catalytic cycle. Several transformations of one of the products were also demonstrated.

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