Asymmetric Synthesis of Eight-Membered *N*-Heterocycles: Auto-organocatalyzed Ring Expansion of Tetrahydrocarbolines with Kinetic Resolution

([1]*SANKEN, Osaka University,* [2]*Graduate School of Science and Engineering, Ibaraki University*)
○Tin Zar Aye,[1] Masaru Kondo,[1,2] Shinobu Takizawa,[1] Hiroaki Sasai[1]
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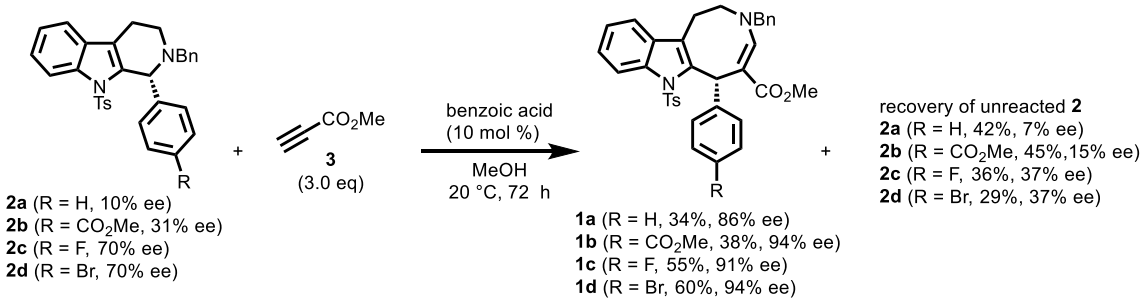
Chiral tetrahydroazocinoindoles are a structural fragment in many alkaloids displaying a broad range of biological activity. Although the major efforts by synthetic organic chemists have been directed toward the development of methods to synthesize analogs of natural products,[1] few asymmetric syntheses of tetrahydroazocinoindoles have been reported to date. In this work, we report the first asymmetric synthesis of tetrahydroazocino[5,4-b]indoles *via* autocatalytic ring expansion with kinetic resolution. We found that asymmetric autocatalysis on ring expansion of 10-70 % ees of tetrahydro-β-carbolines[2] **2** with methyl propiolate (**3**) produced tetrahydroazocino[5,4-b]indole **1** in 34 to 60% yields and up to 94% ee without using any chiral catalyst, together with recovery of unreacted **2** in 29 to 42% yields with 7 to 37% ees.



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