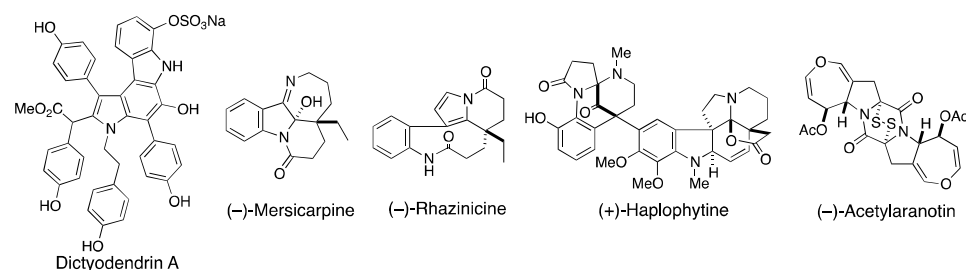


## Synthetic Studies on N-Heterocyclic Natural Products

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Since nitrogen-containing heterocyclic rings are common structural motifs in biologically important natural products, development of new synthetic methodologies for construction of these structures have been one of the important research topics in synthetic chemistry. In this lecture, our recently completed total syntheses of polycyclic alkaloids featuring new synthetic strategies will be discussed. We investigated a reductive ring expansion of cyclic ketoximes and applied to a concise total synthesis of (-)-mersicarpine.<sup>1</sup> For formation of substituted indolines, we developed a benzyne-mediated cyclization-functionalization sequence and applied this reaction to total syntheses of dictyodendrins A-E.<sup>2</sup> A protective group free total synthesis of (-)-rhazinicine was accomplished based on the development of a gold-catalyzed double cyclization cascade.<sup>3</sup> In the first total synthesis of (+)-haplophytine, we constructed the characteristic spiroaminal by an oxidative semi-pinacol type rearrangement.<sup>4</sup> Dihydrooxepin rings in (-)-acetylaranotin was formed by combination of the vinylogous Rubottom oxidation and the Baeyer-Villiger ring expansion of an enone intermediate.



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