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Title:	New Strategies to Synthesize Small and Medium sized Rings Bearing a Stereogenic Center
Authors:	<a href="#">Singh, Bara</a>
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Abstract:	<p>Cyclic molecular frameworks hold a special place in the chemical world. Carbo- and heterocyclic compounds comprising small and medium-sized rings with a stereogenic center are pertinent in organic chemistry. The importance of scaffolds containing tertiary, all-carbon quaternary, or spiro centers in synthetic chemistry, organic functional materials, and pharmaceuticals necessitates the development of innovative methodologies to access them in a broad, efficient, and atom-economic manner. The thesis' content has been divided into three chapters. In chapter 1, we described the first neutral Pd-catalyzed Nazarov-type cyclization of allyl acetates to synthesize various indanes possessing a tertiary stereocenter and a diverse range of cyclopenta[b]annulated heteroarenes. This approach allows easy access to numerous types of bi-, tri-, tetra-, and pentacyclic cyclopentanoids. The first total synthesis of <math>\square</math>-diasarone and several other complex cyclopentanoids pertinent to medicinal chemistry and material research further demonstrates the synthetic value. Next, in chapter 2, we developed an unprecedented Pd(II)-promoted 5-endo-trig carbocyclization similar to acid-free Nazarov-type cyclization to synthesize fused cyclopentenones with an all-carbon quaternary/spiro center. The reaction demonstrated remarkable functional group tolerance with electronically varied substituents, allowing good to excellent yields of spirocyclopentene oxindoles, cyclopentene-fused arenes, and heteroarenes. Natural products (such as taiwaniaquinoids), and pharmaceutically relevant compounds were synthesized efficiently without any external oxidant, base, addition, or ligand, demonstrating the method's generality and practicability. Finally, in chapter 3, we developed a set of diastereoselective cyclopropanoids utilizing a hybrid strategy based on azaarenium salts and sulfur ylide. Through an interrupted Corey-Chaykovsky reaction, simultaneous dearomatizing spirannulation of designed azaarenium salts allows access to novel scaffolds with at least three contiguous stereocenters (one being an all-carbon spiro center). This strategy provides efficient routes to access functionally-rich bispirocyclic indanones and spirannulated benzocycloheptanones in good to excellent yields.</p>
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