

## Abstract

This work consists of four consecutive parts, each dealing with syntheses of structurally diverse compounds. The syntheses were based on the methods within the domain of transition–metal catalyzed and/or mediated reactions with particular emphasis on the application of organozirconium chemistry.

1. A method for synthesis of tricyclic condensed hydrocarbons possessing 5(6)–7–6(aryl) framework was developed. It is based on reaction of bicyclic zirconacyclopentenes, prepared by oxidative dimerization of enynes on a low–valent zirconocene species (Negishi's reagent), with *ortho*–halobenzaldehydes in the presence of various additives. The presence of two different centers of reactivity – the  $sp^2C$ –Zr and  $sp^3C$ –Zr bond – allowed sequential functionalization of each bond. Thanks to its higher nucleophilicity, the  $sp^3C$ –Zr bond reacted preferentially with the carbonyl carbon of the aldehyde yielding an oxazirconacycloheptene. The subsequent transmetallation of the remaining  $sp^2C$ –Zr bond with CuCl in the presence of other additives (catalysts) enabled an intramolecular cross–coupling reaction with the aryl halide moiety furnishing the desired tricyclic products in reasonable yields. The scope of the reaction with respect to differently functionalized reactants was assessed, as well as its mechanistic aspects were studied in detail. In conclusion, this approach provided a simple and one–pot procedure for the synthesis of the fused 5(6)–7–6(aryl) ring compounds.

2. A new method for synthesis of carbocyclic compounds featuring fused 5–8, 6–8 ring systems was developed. The method was based on the reaction of bicyclic zirconacyclopentenes, easily prepared from the corresponding enynes and Negishi's reagent, with excess of allyl chloride in the presence of a catalytic amount of copper(I) chloride that gave rise to 1,9–decadienes. The subsequent Ru–complex catalyzed ring–closing metathesis of the dienes afforded the compounds possessing the fused 5(6)–8–membered ring systems. In addition, the selective mono–allylation of the  $sp^2C$ –Zr bond of a bicyclic zirconacyclopentene was achieved and followed by introduction of a different functionality at the remaining  $sp^3C$  atom. This allowed development of an alternative pathway for synthesis of the 5–8–membered ring carbocycles possessing the functionalized 8–membered ring.

3. Attempts to utilize zirconocene-mediated cyclization of appropriately substituted enynes for synthesis of the advanced building block enroute to astericanolide were not met with success. An alternative approach to cyclization based on the use of low-valent titanium species did not also lead to the desired products. Although this part of the PhD project was not successful, it provided valuable data that could be utilized in future attempts of asteriscanolide synthesis.

4. A new three-step synthesis of selectively 1,2-disubstituted cyclopentadienes utilizing catalytic transformations of alkynes was developed. The synthesis was based on i) Pd-catalyzed bromoallylation of internal alkynes, ii) Pd-catalyzed cross-coupling with vinyl metals and iii) Ru-catalyzed ring-closing metathesis. Cyclopentadienyl anions, prepared by metalation of selected cyclopentadienes, were then converted to the corresponding ferrocenes, cymantrene, and cyrhetrenes by reactions with the respective iron, manganese or rhenium salts.