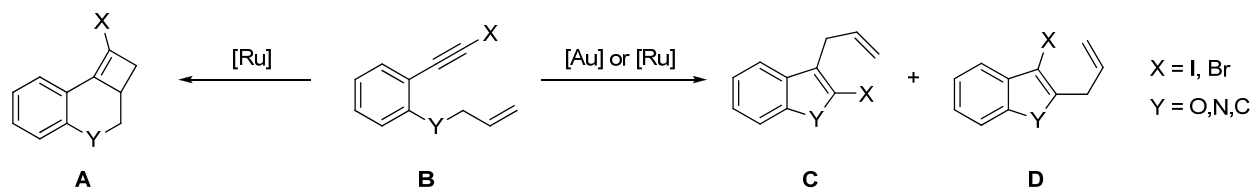


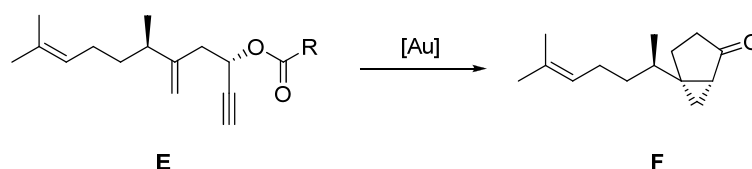
During the last two decades metal-catalysed cycloisomerisations have become an important tool for the construction of small, often bi- or polycyclic systems. Within this realm the cycloisomerisation of 1,7-enynes **B** bearing a halide at the triple bond, and the cycloisomerisation of 1,5-enynes towards [3.1.0]-bicyclic systems is described.

1,7-Enynes **B** can be converted into benzofurans and indoles **C** and **D**. The selectivity of the reaction is dependent on the catalyst applied. Au(I)-based catalysts form preferentially the 3-halide-substituted product with ratios of **C/D** around 1/3.5. This system is relatively tolerant towards variation of the substrate. Ru-based catalysts invert the product ratio in favour of **C** when CO is present. Selectivities and yields are heavily dependent on the substrate architecture.



Cyclobutenes **A** are formed in the presence of  $\text{RuCp}^*(\text{MeCN})_3\text{PF}_6$ . This transformation is very robust against variations on the substrate backbone. Therefore, not only tricyclic, but also bi- and tetracyclic systems can be assembled. The reaction is in most cases diastereoselective and allows for the formation of O-, N- and purely carbocyclic products. The cycloisomerisations are selective for 1,7-enynes bearing bromo- or iodo-substituents at the triple bond.

The Ohloff–Rautenstrauch-reaction of 1,5-enynes was applied for the construction of [3.1.0]-bicyclic systems, that are common subunits of sesquiterpenes. In this work a diastereoselective procedure for the Ohloff–Rautenstrauch-reaction was developed and the obtained product **F** was converted into 11 different natural products; 10 of them had not been synthesised before and thitherto not been stereochemically assigned.



Furthermore in course of the synthesis of **E** a diastereoselective allylation of propargylic aldehydes using Ph-BOX ligands was developed.