Total Synthesis of Isoflavonoids by PtCl₂-Catalyzed Carboalkoxylation

Novel User-Friendly Catalysts for the Alkyne Metathesis

A total synthesis of the pterocarpene derivative erypoegin H has been devised. This isoflavonoid has been recently isolated from *Erythrina poeppigiana* and possesses bactericidal activity against a range of methicillin-resistant Staphylococcus aureus (MRSA) and vancomycin-resistant *enterococci*. The application of a PtCl₂-catalyzed carboalkoxylation of alkynes as the key step afforded not only a quick access to erypoegin H in high yields, but also led to the synthesis of its cognates sojagol and phaseol.

Furthermore, a novel user-friendly *in situ* generated catalyst for alkyne metathesis has been developed. Mixing trichloro molybdenum nitride (NMoCl₃) and lithium triphenylsilanolate (Ph₃SiOLi) forms a species which performs cross alkyne metathesis (CAM) as well as ringclosing alkyne metathesis (RCAM). The tolerance of a broad range of functional groups including esters, ethers, amides, carbamates, thiophenes, thioethers and sulfones was shown. The employment of propargylic ethers was also demonstrated for the first time in an alkyne metathesis. This new substrate class was used in a CAM as a key step for a concise total synthesis of gallicynoic acid I.