



Tris(triphenylphosphine) Ruthenium(II) dichloride : a versatile catalyst in the synthesis of (Sb(B-), (Sd(B- and (Se(B-lactams from trichloroacetamides and in the isomerization of protected allylamines to Z-enamines under microwave activation

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Tesis doctorals electròniques

Monografía

"In this PhD thesis we have demonstrated that tris(triphenylphosphine)ruthenium(II) dichloride ($\text{RuCl}_2(\text{PPh}_3)_3$) is a potent and versatile catalyst capable of achieving efficient different chemical transformations under microwave activation. In the first part of this PhD thesis, we have reported an expeditious synthesis of (Sb(B--lactams from N-tethered benzyl trichloroacetamides in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ and under microwave activation. The new $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ bond formation takes place through an unprecedented "Ru" complex promoted activation of a benzylic position in a radical process. The methodology was applied on 10 examples with acceptable yields considering the challenging C-C bond formed in this radical process. Of the (Sb(B-lactams prepared, 6 were analyzed for their cytotoxic activity and hemocompatibility. The results obtained showed that these lactams have non-hemolytic character and that their cytotoxic response is highly dependent on their structural characteristics and their concentration. One of the compounds tested was found to be the most cytotoxic showing the lowest IC_{50} values. In the second part of the thesis, we have reported the first isomerization of tertiary allylcarbamates and allylamides to the corresponding Z-enecarbamates and Z-enamides in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ as a catalyst with very good yields and excellent Z-selectivity. The reactions are achieved under microwave activation and in very short reaction time on different substrates. In this transformation we have demonstrated that the nature of the protective group on the nitrogen is decisive to the course of the reaction. Finally, the same catalyst was used for the synthesis of (Sd(B- and (Se(B-lactams from N-tethered alkenyl trichloroacetamides. In this part of the work, a reliable diastereoselective Atom Transfer Radical Cyclization takes place in the presence of a catalytic amount of $\text{RuCl}_2(\text{PPh}_3)_3$ to provide the

corresponding lactams with good yields. The methodology was successfully used for a diastereoselective synthesis of functionalized indole and morphan scaffolds present in many natural compounds such as the Daphniphyllum alkaloids." -- TDX

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