

Palladium-Catalyzed Amino-carbonylation and Alkoxy Carbonylation Reactions of Phenyl Acetylene with Bifunctional N, O- Amino-Alcohols: Highly Chemo- and Regioselective Synthesis of α,β -Unsaturated Amide Esters

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Abstract

This work reports the chemo- and regio-selective direct palladium-catalyzed aminocarbonylation and alkoxy carbonylation of phenyl acetylene, utilizing an aminoethanol and other various amino-alkanols as a bifunctional N, O nucleophile to synthesize hydroxy-substituted, α,β -unsaturated amides, imides, and amide esters in good to excellent yields by varying various catalyst precursors, ligands, and other conditions. This work focuses on good to excellent chemo- and regio-selectivity towards amide esters since they have the ability to combine the best properties of polyesters (flexibility) and polyamides (strength/rigidity) therefore very crucial in biotechnology, materials science, and pharmaceuticals. By a simple variation in ligands and additives, branched-branched or branched-linear isomers of amide-esters could be selectively formed with excellent regioselectivity. When a quantitative amount of p-toluene sulphonic acid (PTSA/ p-TsOH·H₂O) was applied as an additive at an optimized pressure of CO at 40 bars, Branched-linear amide esters were produced in relatively excellent yields and selectivities using (R)-1-[(S_P)-2-(Diphenylphosphino)ferrocenyl]ethyldicyclohexylphosphine (DPFEDicycloP) as the ligand. On the other hand, Branched-branched amide esters could be approached by introducing a quantitative amount of benzoic acid as the additive at an optimized pressure of CO at 10 bars. Useful reaction scope with various amino alcohols and alkynes were performed leading to synthesis of important targeted compounds.

Index Terms

Aminocarbonylation, Bi-functional N,O-Nucleophile, α,β -unsaturated amide-esters, Regioselectivity, Palladium-Catalysis