Total regioselective control of the carbonylative coupling of 1-heptyne with aniline and N-methylaniline catalyzed by palladium(II) and phosphine ligand.
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Abstract

The regioselective carbonylative coupling of aniline to 1-heptyne was achieved successfully using the catalytic system A formed of Pd(OAc)$_2$/1,3-bis(diphenylphosphino)propane/p-toluenesulfonic acid with CO in THF and the system B consisting of Pd(OAc)$_2$/1,4-bis(diphenylphosphino)butane/CO/H$_2$/CH$_2$Cl$_2$. The gem-$\alpha,\beta$-unsatd. amide was formed as a predominant product in the presence of the catalytic system A. The system B provided an efficient and simple method for the synthesis of trans-$\alpha,\beta$-unsatd. amide. The reaction of N-methylaniline with 1-heptyne also gave excellent yields and selectivity of the tertiary gem- and trans-$\alpha,\beta$-unsatd. amides.