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Title: Pd(II)-Catalyzed Bidentate Directing Group-Aided Chemoselective Acetoxylation of Remote ϵ -

C(sp2)-H Bonds in Heteroaryl-Aryl-Based Biaryl Systems

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Abstract:

In this Article, we report our successful attempt on the Pd(II)-catalyzed, bidentate directing group-aided, chemoselective acetoxylation/substitution of remote $\epsilon\text{-}C(sp2)\text{--}H$ bonds using heteroaryl-aryl-based biaryl systems. While the bidentate directing group (BDG)-aided, C–H activation, and functionalization/acetoxylation of the $\beta\text{--}, \gamma\text{--},$ and $\delta\text{--}C\text{--}H$ bonds of the appropriate carboxamide systems were well documented, there exist only rare reports dealing with the C–H activation and functionalization of remote $\epsilon\text{--}C\text{--}H$ bonds of appropriate substrates. Especially, the BDG-aided chemoselective acetoxylation of the remote $\epsilon\text{--}C(sp2)\text{--}H$ bond over cyclization has not been explored well. Accordingly, in this work, the treatment of various

picolinamides/oxalylamides/pyrazine-2-carboxamides 4/7/9/11, which were derived from the corresponding C-3 arylated furfurylamines or thiophen-2-ylmethanamines with PhI(OAc)2 in the presence of the Pd(OAc)2 catalyst, successfully afforded the corresponding ϵ -C-H acetoxylated products. The chemoselective acetoxylation of the ϵ -C-H bond was possible and facilitated by the

biaryl substrate 4/7/9/11 and not by the biaryl substrate 2a.

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