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Title: 4-Amino-2,1,3-benzothiadiazole as a Removable Bidentate Directing Group for the Pd(II)-

Catalyzed Arylation/Oxygenation of sp2/sp3 β-C-H Bonds of Carboxamides

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Directing group Pd(II)-catalyzed

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Abstract: In this paper, we report 4-amino-2,1,3-benzothiadiazole (ABTD) as a new bidentate directing group

for the Pd(II)-catalyzed sp2/sp3 C-H activation/functionalization of various

aliphatic/alicyclic/aromatic carboxamide systems. The Pd(II)-catalyzed, ABTD-directed sp3 C–H arylation/acetoxylation of aliphatic- and alicyclic carboxamides afforded the corresponding  $\beta$ -C–H arylated/acetoxylated carboxamides. The Pd(II)-catalyzed, ABTD-directed sp3 C–H arylation of cyclobutanecarboxamide with different aryl iodides afforded the corresponding bis  $\beta$ -C–H arylated cyclobutanecarboxamides having all-cis stereochemistry with a high degree of stereocontrol. The Pd(II)-catalyzed, ABTD-directed arylation/benzylation/acetoxylation/alkoxylation of ortho C(sp2)–H

bonds of various benzamides afforded the corresponding ortho  $C\!-\!H$ 

arylated/benzylated/oxygenated benzamides. The observed regio- and stereoselectivity in the Pd(II)-catalyzed, ABTD-directed arylation/benzylation of aliphatic/alicyclic carboxamides and benzamides were ascertained from the X-ray structures of representative compounds 5g (bis-β-C(sp3)–H arylated cyclobutanecarboxamide) and 7f (ortho C(sp2)–H arylated benzamide). A brief description on the efficiency, scope, and limitations of bidentate directing group ABTD is reported.

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