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Title: Utility of 4-Amino-2,1,3-benzothiadiazole Directing Group in the Pd(II)-catalyzed Arylation of γ-

C-H Bonds of Carboxamides and β-C-H Bonds of Amino Acid Carboxamides

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Keywords: Utility of 4-Amino-2,1,3-benzothiadiazole

Pd(II)-catalyzed Arylation γ-C-H Bonds of Carboxamides

β-C-H Bonds of Amino Acid Carboxamides

Issue Date: 2022

Publisher: John Wiley & Sons

Citation: Asian Journal of Organic Chemistry, 11(12), 589.

Abstract:

Expanding the availability, scope, and limitations of directing groups (DGs) for executing the siteselective C-H activation and functionalization and substrate scope development are valuable efforts. This paper reports the scope and extension of the utility of the 4-amino-2,1,3benzothiadiazole (ABTD) directing group in the Pd(II)-catalyzed arylation of remote sp2/sp3 γ-C-H bonds of aromatic carboxamides and sp3 β-C-H bonds of amino acid carboxamides. The performance of the ABTD DG in the arylation of remote γ -C-H bonds of carboxamides and sp3 β -C-H bonds of amino acid carboxamides was compared with other known DGs. For example, we have observed that the mono arylation of the methyl sp3 β-C-H bonds of alanine carboxamide possessing the ABTD DG with iodopyridine yielded the pyridylalanine derivative. Conversely, the same reaction using 8-AQ DG did not yield the expected pyridylalanine derivative. Furthermore, 2,1,3-benzothiadiazole moiety-containing compounds are an important class of molecules in materials chemistry and medicinally relevant molecules. While this work reveals the utility of ABTD as the DG in the Pd(II)-catalyzed C-H arylation of carboxamides including amino acid derivatives. On the other hand, indirectly the process of ABTD-aided C-H arvlation reactions has enabled to accomplish the synthesis of a library of 2,1,3-benzothiadiazole moiety containing new carboxamides.

Description: Only IISER Mohali authors are available in the record.

URI: https://doi.org/10.1002/ajoc.202200589 (https://doi.org/10.1002/ajoc.202200589) http://hdl.handle.net/123456789/5155 (http://hdl.handle.net/123456789/5155)

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