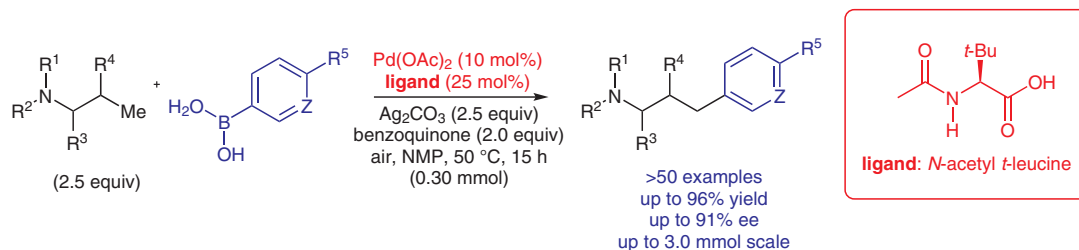


J. RODRIGALVAREZ, M. NAPPI, H. AZUMA, N. J. FLODÉN, M. E. BURNS, M. J. GAUNT*
(UNIVERSITY OF CAMBRIDGE, UK)

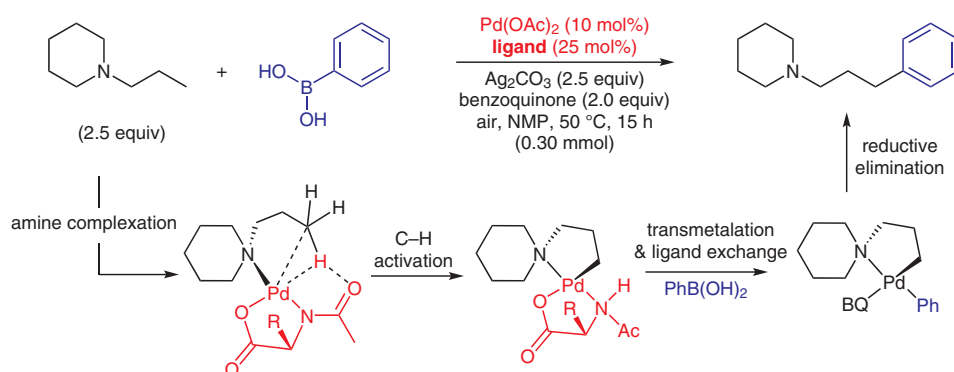
Catalytic C(sp³)-H Bond Activation in Tertiary Alkylamines

Nat. Chem. 2020, 12, 76–81.

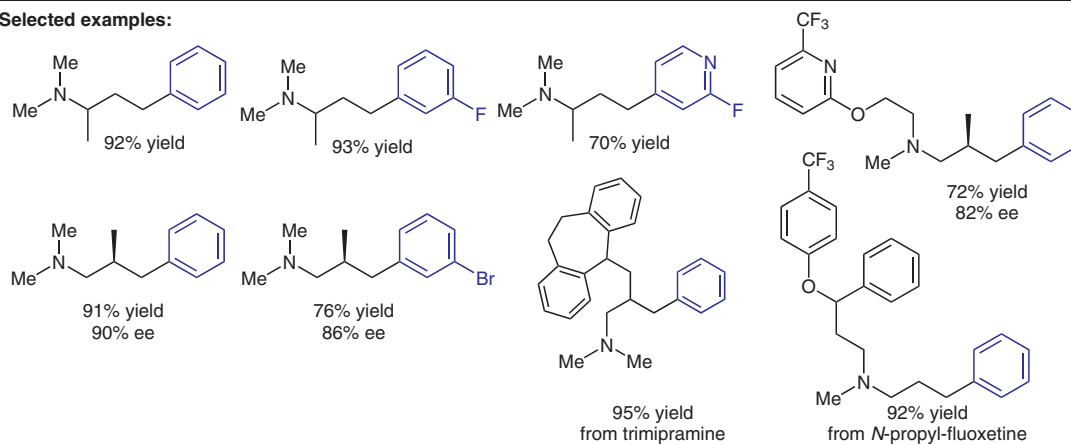
Palladium-Catalyzed γ -C(sp³)-H Bond Activation of Tertiary Alkyl Amines



Proposed reaction mechanism of γ -C(sp³)-H arylation:



Selected examples:



Significance: Gaunt and co-workers report a novel ligand-enabled palladium(II)-catalyzed γ -C(sp³)-H arylation. Selective functionalization of tertiary alkyl amines is observed utilizing arylboronic acids under mild conditions. The reaction is enantioselective, with enantiotopic methyl group differentiation, allowing efficient and selective access to γ -aryl tertiary amine scaffolds.

Comment: The authors propose that the reaction proceeds by amine complexation to the palladium(II) ligand complex, followed by a concerted ligand-assisted metalation-deprotonation process to access the palladacycle. This intermediate then undergoes transmetalation with the boronic acid, which then undergoes a reductive elimination to afford the product.

SYNFACTS Contributors: Mark Lautens, Randy Sanichar
Synfacts 2020, 16(04), 0411 Published online: 18.03.2020
DOI: 10.1055/s-0040-1707645; Reg-No.: L02720SF

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Category

Metals in Synthesis

Key words

palladium catalysis

regioselectivity

C-H activation

γ -aryl tertiary amines

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