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

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.