Tahmina Afroz

SRS (Abstract)

Tuning Iron-Based Macrocyclic Catalysts for Efficient C–C Coupling

Our study investigated high-spin iron/tetra-aza macrocyclic complexes as sustainable catalysts for Suzuki–Miyaura C–C coupling, demonstrating ligand modifications as key regulators of catalytic activity. Initial findings showed that ligand modifications influenced yields but could not separate redox effects from geometry. Later studies on PyN_3 confirmed that 4-substituted pyridine ligands provide direct electronic control, with EWGs boosting yields and EDGs reducing efficiency due to dimer formation. A comparative analysis revealed that $Fe^{III}(RPy_2N_2)^{3+}$ outperformed $Fe^{III}(RPyN_3)^{3+}$ by at least 10%, highlighting scaffold design as a key determinant of activity. Substrate scope showed broad functional group tolerance (43–78% yields), and mechanistic studies identified an iron(III)-hydroperoxo species as the active oxidant, ruling out a Fenton-type radical pathway. These findings establish iron-based macrocyclic catalysts as a tunable and sustainable alternative to palladium for direct arylation of un-activated arenes.