

Iron-Catalyzed Regioselective Thienyl C–H/C–H Coupling and Polycondensation

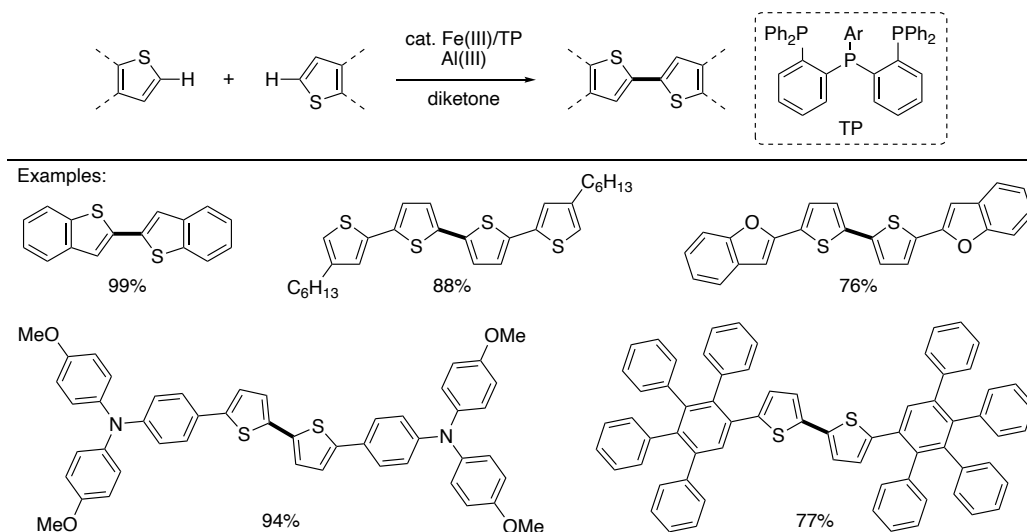
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Direct C–H/C–H coupling to connect two aromatic molecules has attracted attention as one of the most straightforward methods to synthesize biaryls. However, such methods reported so far require strongly oxidizing conditions either to generate reactive cationic radical species (e.g. Scholl reaction, oxidative aromatic coupling)¹ or to turnover catalyst (e.g. palladium catalysis)², which limit their synthetic versatility.

Herein, we report that iron(III)/tridentate phosphine catalyst³ in combination with AlMe₃ and a latent oxidant, diketone, enables efficient and selective thienyl C–H/C–H coupling under mildly oxidative conditions. Furthermore, thienyl C–H/C–H polycondensation, which requires high catalytic efficiency, was achieved by the use of a newly designed tridentate phosphine ligand with a modification on the central aryl group. The reaction is compatible with various π -motifs found in optoelectronic materials and allows direct synthesis of dimeric, oligomeric, and polymeric thiophene materials of importance in energy device applications from simple thiophene C–H substrates.



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