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Micellar Catalysis: A Green Solution to Enable Undirected and Mild C-H Activation of (Oligo)thiophenes at the Challenging β -Position

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Intramicellar Pd-Catalyzed β-Arylation of Thiophenes

$$\begin{array}{c} \text{Pd(OAc)}_2 \text{ (10 mol\%)} \\ \text{AgOAc (1.0 equiv)} \\ \text{PS-750-M (3 wt\% in H}_2\text{O)} \\ \text{undecanoic acid (1.0 equiv)} \\ \text{under air, r.t., 16 h} \\ \text{p99\% yield (NMR)} \\ \text{p100 PS-750-M} \\ \text{p99\% yield (NMR)} \\ \text{p100 PS-750-M} \\ \text{p100 PS-750-M} \\ \text{in situ} \\ \text{in situ} \\ \text{p100 PS-750-M} \\ \text{in situ} \\ \text{p100 PS-750-M} \\ \text{in situ} \\ \text{p100 PS-750-M} \\ \text{p100 PS-750-M} \\ \text{p100 PS-750-M} \\ \text{in situ} \\ \text{p100 PS-750-M} \\ \text{p10$$

Significance: Palladium-catalyzed C–H arylation of thiophenes with aryl iodides was found to proceed with 'unusual' β-position selectivity in the presence of a proline-based surfactant PS-750-M. The arylation of a wide variety of (oligo)thiophenes was carried out with 10 mol% of Pd(OAc)₂ in a three wt% aqueous solution of PS-750-M in the presence of silver acetate and undecanoic acid at room temperature to give the corresponding β-arylated thiophenes with excellent regioselectivity.

Comment: The amphiphilic proline-based surfactant PS-750-M formed micelles in situ under the reaction conditions. The authors proposed that the arylation took place inside the micelles. Undecanoic acid significantly accelerate the arylation. The arylation did not proceed in the absence of silver acetate.

Category

Polymer-Supported Synthesis

Key words

micelle
palladium catalysis
thiophenes
C-H arylation

