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C2-Selective Arylation of Indoles with Heterogeneous Nanopalladium and Diaryliodonium Salts
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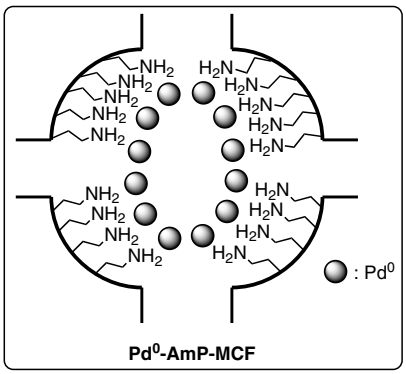
Category

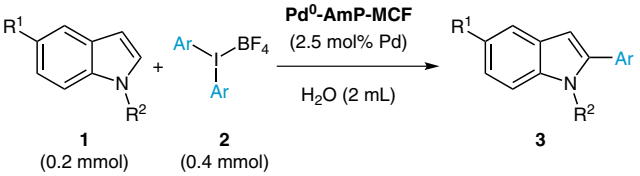
Polymer-Supported Synthesis

Key words

arylation
diaryliodonium salts
indoles
palladium catalysis

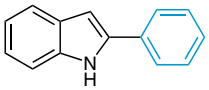
A Heterogeneous Palladium Catalyst for C2-Selective Arylation of Indoles



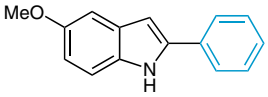


1 (0.2 mmol) **2** (0.4 mmol) **3**

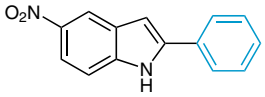
Selected results:



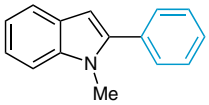
3a
R^1 = H, R^2 = H, Ar = Ph
r.t., 6 h, 91% yield



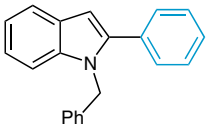
3b
R^1 = MeO, R^2 = H, Ar = Ph
40 °C, 6 h, 86% yield



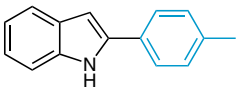
3c
R^1 = NO_2, R^2 = H, Ar = Ph
50 °C, 25 h, 70% yield



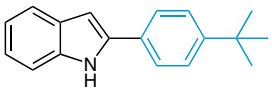
3d
R^1 = H, R^2 = Me, Ar = Ph
r.t., 6 h, 80% yield



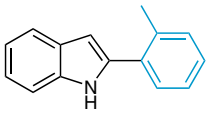
3e
R^1 = H, R^2 = MeC_6H_5, Ar = Ph
50 °C, 24 h, 65% yield



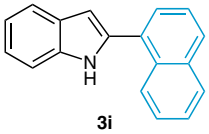
3f
R^1 = H, R^2 = H, Ar = 4-MeC_6H_4
40 °C, 6 h, 83% yield



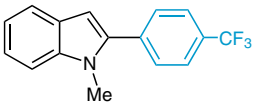
3g
R^1 = H, R^2 = H, Ar = 4-*t*-BuC_6H_4
r.t., 15 h, 84% yield



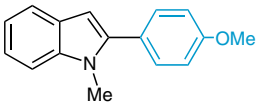
3h
R^1 = H, R^2 = H, Ar = 2-MeC_6H_4
40 °C, 6 h, 76% yield



3i
R^1 = H, R^2 = H, Ar = Np
40 °C, 15 h, 67% yield



3j
R^1 = H, R^2 = Me, Ar = 4-$F_3CC_6H_4$
40 °C, 15 h, 99% yield



3k
R^1 = H, R^2 = Me, Ar = 4-$MeOC_6H_4$
40 °C, 6 h, 72% yield

Significance: Pd^0-AmP-MCF constitutes of silica-based mesocellular foam (MCF) functionalized with aminopropylsilane (for the preparation, see: M. Shakeri et al. *Chem. Eur. J.* **2011**, *17*, 13269). Pd^0-AmP-MCF (palladium particles ø: 2–3 nm) catalyzed the C2-selective arylation of indoles **1** and substituted diaryliodonium tetrafluoroborates **2** to give the corresponding indole derivatives in 65–99% yield (15 examples).

Comment: The reactions of an electron-rich indole (**3b**), an N-methylated indole (**3d**), *para*-alkyl-substituted salts (**3f**,**g**), or an electron-deficient CF_3-substituted salt (**3j**) afforded high yields, whereas an N-benzylated indole (**3e**) or a naphthyl salt (**3i**) resulted in lower yield. ICP-OES analysis showed 0.6 ppm of palladium leaching from the reaction mixture (**3a**).

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