

Category

Synthesis of
Materials and
Unnatural Products

Key words

fluorenones

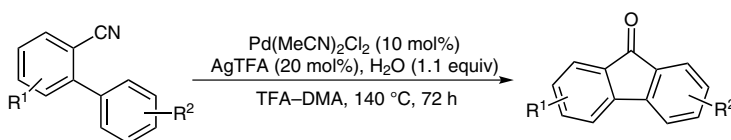
palladium

C–H activation

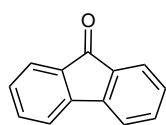
J.-C. WAN, J.-M. HUANG, Y.-H. JHAN, J.-C. HSIEH* (TAMKANG UNIVERSITY, NEW TAIPEI CITY, TAIWAN)

Novel Syntheses of Fluorenones via Nitrile-Directed Palladium-Catalyzed C–H and Dual C–H Bond Activation
Org. Lett. **2013**, *15*, 2742–2745.

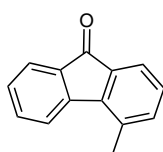
Nitrile-Directed Palladium-Catalyzed Syntheses of Fluorenones



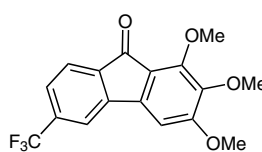
Selected examples:



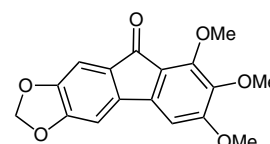
82% yield



90% yield

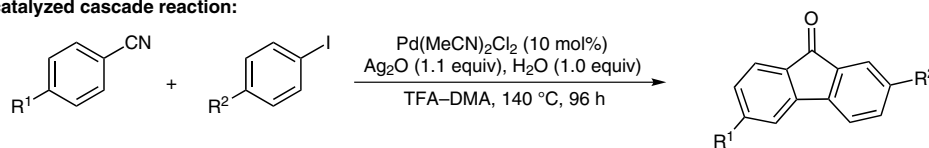


79% yield

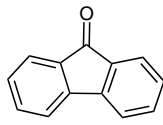


43% yield

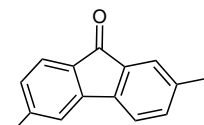
Pd-catalyzed cascade reaction:



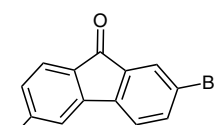
Selected examples:



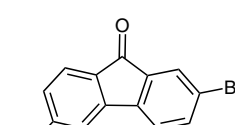
67% yield



53% yield



50% yield



32% yield

Significance: Two new synthetic strategies for the palladium-catalyzed synthesis of fluorenones are discussed. Both strategies rely on nitrile-directed C–H bond activation. The first involves C–H activation of a 2-arylbenzonitrile followed by insertion of the nitrile, whereas the second is a dual cascade reaction between a substituted benzonitrile and aryl iodide. Several substituted fluorenones with various substituents were synthesized with both methods.

Comment: In addition to their major results, the authors report the optimization of their catalytic system and discuss the selectivity of fluorenone formation over competing side reactions in certain substrates. Based on additional observations and experiments, a mechanism for the dual C–H activation approach is also proposed. The authors note that they are currently investigating the application of these reported strategies to other chemical transformations and the synthesis of natural products.

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Synfacts 2013, 9(9), 0948 Published online: 19.08.2013
DOI: 10.1055/s-0033-1339627; **Reg-No.:** S07613SF

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