

SYNFACTS Highlights in Current Synthetic Organic Chemistry

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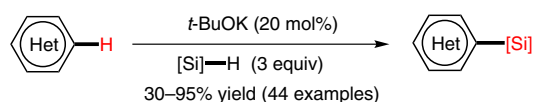
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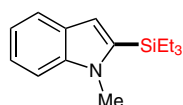
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A. A. TOUTOV, W.-B. LIU, K. N. BETZ, A. FEDOROV, B. M. STOLTZ,* R. H. GRUBBS* (ETH ZÜRICH, SWITZERLAND AND CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, USA)
Silylation of C–H Bonds in Aromatic Heterocycles by an Earth-Abundant Metal Catalyst
Nature 2015, 518, 80–84.

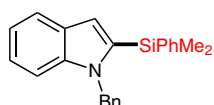
Silylation of Aromatic Heterocycles with Potassium *tert*-Butoxide Catalyst



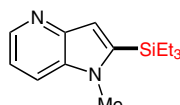
Selected examples:



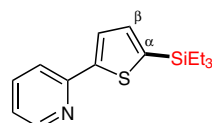
Neat, 45 °C
C2/C3 > 20:1
78% yield



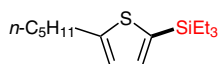
THF, 45 °C
C2/C3 > 20:1
58% yield



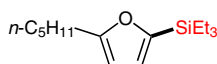
THF, 45 °C
C2/C3 = 6:1
33% yield



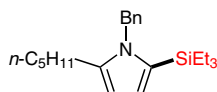
THF, 25 °C
 α/β > 20:1
83% yield



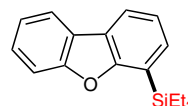
t-BuOK (1 mol%)
5 mmol scale
THF, 25 °C
 α/β > 20:1
92% yield



73 mmol scale
THF, 25 °C
 α/β > 20:1
95% yield



THF, 25 °C
mono/bis = 10:1
80% yield



THF, 65 °C
o/p > 20:1
mono/bis = 15:1
71% yield

Significance: The authors report the direct C–H bond silylation of aromatic heterocycles using potassium *tert*-butoxide, an inexpensive and readily available catalyst. The reaction proceeds under mild conditions, with good yields, high selectivity, and high scalability. It works on a broad range of heterocycles and is more effective on electron-neutral and -rich systems. Silylation of sp^3 carbons has also been observed.

Comment: This reaction is a valuable addition to existing silylation methods, without the need for prefunctionalization of heteroarenes, ligands, or additives. The heteroarylsilane products are important in medical and material applications. In addition, the silane group can be easily converted into other functional groups, some of which have been demonstrated in the paper. The extension of this method to non-aromatic systems and mechanistic studies are in progress.

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