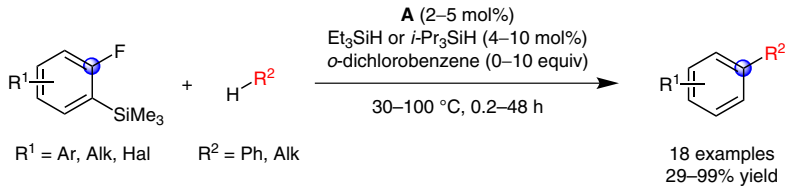
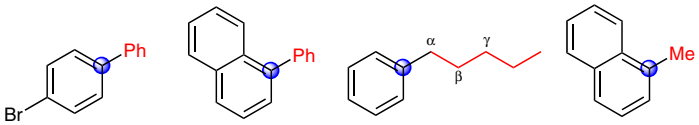
B. SHAO, A. L. BAGDASARIAN, S. POPOV, H. M. NELSON* (UNIVERSITY OF CALIFORNIA, LOS ANGELES, USA)

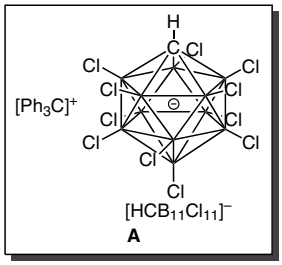
Arylation of Hydrocarbons Enabled by Organosilicon Reagents and Weakly Coordinating Anions
Science **2017**, *355*, 1403–1407.

Silylium Ion Catalyzed C–H Arylation of Hydrocarbons

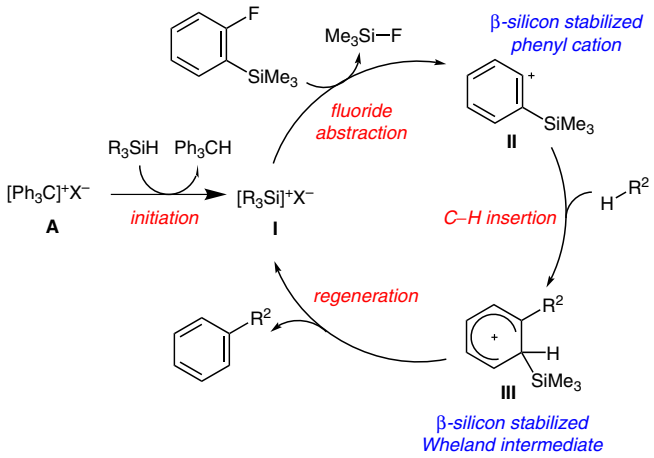


Selected examples:





Proposed catalytic cycle:



Significance: The Nelson group reports a silylium ion catalyzed arylation of C(sp^2)–H and C(sp^3)–H bonds. By employing 2–5 mol% of precatalyst **A** in the presence of a trialkylsilane initiator, various aliphatic and aromatic hydrocarbons were arylated with variously functionalized trimethylsilyl fluorobenzenes.

Comment: Previously, catalytic reactions involving highly reactive phenyl cation equivalents were limited to intramolecular transformations. The authors describe the formation of a β-silicon-stabilized phenyl cation (equivalent) **II**, which is proposed to subsequently undergo intermolecular insertion into the C–H bond of a hydrocarbon present in large excess. Desilylation of the resulting Wheland intermediate furnishes the product and regenerates the catalytically active species **I**.

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Synfacts 2017, 13(06), 0645 Published online: 16.05.2017
DOI: 10.1055/s-0036-1590436; **Reg-No.:** B04017SF

Category
Organo- and Biocatalysis

Key words
arylation
hydrocarbons
phenyl cation
silylium ion